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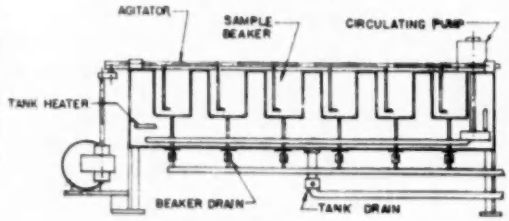

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The Removal of Oils from Textile Materials

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Abstract

The influence of the textile substrate on the detergency process is investigated by straightforward oil removal evaluation in conjunction with contact angle measurements. Difficulty of oil removal is associated with matching of the polarities of oil and fiber which, since oils are at least moderately nonpolar, means that, in general, the more hydrophobic the fiber, the more difficult is oil removal. A general correlation found between detergency and contact angle measurements for liquid paraffin and olive oil implies the adequacy of the "rolling up" mechanism as a description of the detergency process for these oils on assemblies of loose fibers. Discrepancies in the case of two fibers are attributed to the effect of a "capillary displacement" mechanism.

Introduction

There is a vast literature bearing upon the removal of oils from textile materials. Much microscopical evidence has been presented in support of several mechanisms [1, 8, 14, 18, 25, 26, 27, 29], of which only two, "rolling up" and complex formation, can be regarded as being important and of widespread occurrence. The effect of many variables, particularly those relating to the detergent solution, has been systematically investigated and the results explained [3, 16, 18, 19, 21, 24]. There have, on the other hand, been relatively few publications concerned with the effect of the textile substrate on the detergency process, and these have usually been of an *ad hoc* nature [7, 22, 28, 29]. There has, however, recently been observed a correlation between detergency and the polarity of the fiber [8, 9].

The object of this work is to gain further insight into the influence of the textile substrate in the detergency process by examining an extensive range of fibers and relating the results to fiber structure. In addition to straightforward detergency experiments, liquid–solid contact angle measurements are made to obtain information about such basic factors as the free energy of the relevant interfaces and the work of displacement of the oil phase from the fiber by the aqueous phase.

Results and Discussion

Lissapol N was the detergent used and liquid paraffin and olive oil were the oils chosen for this investigation. Contact angle measurements were made on the simpler systems (where experimentally possible) as well as on the detergent solution–oil systems so that the latter could be interpreted more analytically. When the contact angle was $< 30°$ or $> 150°$ it was found that the optics of the system were such that the angle could not be measured with

any degree of reliability; it was difficult to distinguish from 0° or 180° respectively. It was, therefore, decided to designate such angles as $< 30°$ or $> 150°$ respectively and to measure accurately only those angles within the range $30° < \theta < 150°$. This is not so serious a deficiency as it seems, for $\cos \theta$ changes only by 0.13 outside this range and most angles $< 30°$ are likely to be zero and those $> 150°$ are likely to be 180°.

Contact Angle Measurements for Water

It was first established, by comparing the observed contact angle on a few fibers with those on monofilaments of the same materials, that there was no appreciable dependence of the contact angle on fiber diameter. The advancing contact angles for water on all the fibers used in the present work are given in Table I. (The advancing position is the relevant one for the aqueous phase in detergency studies.) The calculated work of adhesion of the water to the fibers (W_{FW}) is also given.

$$W_{FW} = \gamma_W(1 + \cos \theta) = \gamma_F + \gamma_W - \gamma_{FW}$$

where γ_W, γ_F, and γ_{FW} are the interfacial tension of the water, the free surface energy of the fiber surface, and the free interfacial energy of the fiber–water interface. W_{FW} is a measure of the strength of bonding of the water to the fiber surface.

TABLE I. Contact Angles Between Water (Advancing) and Fiber and the Calculated Work of Adhesion of Water to the Fibers

	Contact angle, °	Work of adhesion, ergs/cm.²
Calcium alginate	<30	>135
Celafibre—hydrolyzed*	<30	>135
Viscose (bright)	38	129
Viscose (matt)	40	128
Silk	42	126
Fibrolane BX	44	122
Celafibre—surface dissolved with acetone*	46	121
Cotton	47	121
Orlon	48	121
Tricel	52	117
Dynel	61	107
Ardil	61	107
Terylene—surface dissolved with NaOH*	64	104
Nylon	70	97
Terylene	75	91
Thermovyl	88	74
Courlene	92	70

* Treatments described in experimental section.

TABLE II. Contact Angles for Fibers in the Liquid Paraffin–Water System and the Corresponding Calculated Values for the Work of Adhesion of Liquid Paraffin to the Fibers and Difference in Adhesion Energy

Fiber	Contact angle, °	Work of adhesion, ergs/cm.²	Difference in adhesion energy, ergs/cm.²
Courlene	52	94	−36
Ardil	58	83	−25
Terylene	66	82	−24
Terylene—NaOH	68	79	−21
Dynel	69	78	−21
Thermovyl	71	77	−19
Nylon	94	54	4
Cotton	108	40	18
Orlon	117	32	26
Silk	122	27	31
Fibrolane	125	25	33
Tricel	134	17	41
Celafibre—acetone	138	15	43
Celafibre	143	12	46
Viscose (matt)	144	11	47
Celafibre—hydrolyzed	>150	<8	>50
Calcium alginate	>150	<8	>50

Two factors affecting these contact angles cannot be assessed. These are the surface roughness of the fiber and the configuration of atomic groupings in the fiber surface. These omissions are not considered to be serious, however. The agreement of a few of the results with those obtained on smooth films by Ellison and Zisman [4] and the low degree of hysteresis found for all the fibers indicate that the effect of roughness can justifiably be neglected. As for the other factor, it seems reasonable to assume, unless there is evidence to the contrary, that the bulk chemical structure is a fair representation of the surface structure.

The work of adhesion ($= \gamma_W + \gamma_F - \gamma_{FW}$) depends on the surface free energy of the fiber and on the degree of reduction of the surface free energy of water (usually the higher energy surface) by the attractive forces between the two phases. The nonspecific forces of attraction of water to the substrate increase as the polarity of the latter increase and γ_{FW}, therefore, decreases so long as the free surface energy of the fiber does not become higher than that of the water. In addition, the free surface energy of the fiber increases. The work of adhesion, therefore, should increase as the polarity of the fiber increases—as, indeed, the general trend of the results demonstrates. The decrease in the series Orlon–Dynel–Thermovyl–Courlene, for example, illustrates this. The dipole moment of the C—Cl group

is 2.1 Debye units and that of the C−C≡N group is 3.6 units. The occurrence of specific bonding, such as hydrogen bonding, in some instances, can cause deviation from a general polarity–W_{FW} relationship. The differences among the cellulosic fibers could arise from slight differences in the orientation of the molecules. Also, there may be traces of unextracted wax on the cotton.

The structures of the protein fibers are too complex for detailed discussion, but the difference of about 20 ergs/cm.^{2} between the work of adhesion for Ardil and that for silk and Fibrolane can probably be attributed to differences both in the average hydrophilic character of the constituent amino acid residues and in the amount of cross-linking, which can partially inactivate strongly hydrophilic groups.

The slight increase in hydrophilic character achieved when the surface layers of Terylene are dissolved by sodium hydroxide could possibly be due to a difference in orientation of internal molecules, but is more likely to be due to the formation of free hydroxyl and carboxyl groups. The absence of change in Celafibre, whose surface is dissolved by acetone, can more certainly be interpreted as evidence of uniformity of molecular orientation.

Contact Angles in the Liquid Paraffin–Water System

The measured contact angles in the liquid paraffin–water system are given in Table II, as are the corresponding calculated values of the work of adhesion of liquid paraffin to the fibers in the presence of water (W_{OF}) and of the difference in adhesion energy ($A_{WF} - A_{OF}$). These quantities are defined by

$$W_{OF} = \gamma_{OW}(1 + \cos\theta) = \gamma_{OW} + \gamma_{FW} - \gamma_{OF}$$
$$A_{WF} = \gamma_F - \gamma_{WF}$$

and

$$A_{OF} = \gamma_F - \gamma_{OF}$$
$$\therefore A_{WF} - A_{OF} = \gamma_{OF} - \gamma_{WF}$$

The contact angles are measured in the oil phase and with the aqueous phase in the advancing position.

It is seen that, as expected, the calculated work of adhesion, which is a measure of the affinity of the oil for the fiber relative to the affinity of the water for the fiber, decreases, in general, as the fiber becomes more polar. As the fiber becomes more polar, the forces operative between it and the aqueous phase become stronger and tend to more nearly cancel the residual field of force of the water surface. Additionally, an increasing unsatisfied field of force is being developed at the fiber surface in contact with the oil.

Some of the fibers occupy slightly higher positions in Table II than is appropriate to their polarity, as deduced from their chemical structure and the water/air contact angle. Dynel, Terylene, Ardil, and silk are in this category. The explanation may be that, in these cases, the topography of the fiber surface is

TABLE III. Contact Angle, Work of Adhesion of the Oil to the Fiber, and Differences in Adhesion Energies in the System Liquid Paraffin–0.01% Lissapol N

Fiber	Contact angle, °	Work of adhesion, ergs/cm^2.	Difference in adhesion energies, ergs/cm^2.
Cotton	>150	<1.2	>7.7
Viscose (bright)	>150	<1.2	>7.7
Viscose (matt)	>150	<1.2	>7.7
Tricel	>150	<1.2	>7.7
Celafibre	>150	<1.2	>7.7
Celafibre—acetone	>150	<1.2	>7.7
Celafibre—hydrolyzed	>150	<1.2	>7.7
Fibrolane	>150	<1.2	>7.7
Silk	>150	<1.2	>7.7
Terylene—NaOH	148	1.3	7.6
Nylon	147	1.4	7.5
Dynel	145	1.6	7.3
Orlon	143	1.8	7.1
Terylene	142	1.9	7.0
Calcium alginate	139	2.2	6.7
Ardil	133	2.8	6.1
Thermovyl	130	3.2	5.7
Courlene	68	12.2	−3.3

TABLE IV. Contact Angles, Work of Adhesion of the Oil to the Fiber, and Difference in Adhesion Energies in the System Liquid Paraffin–0.2% Lissapol N

Fiber	Contact angle, °	Work of adhesion, ergs/cm.^{2}	Difference in adhesion energies, ergs/cm.^{2}
Cotton	>150	<0.3	>1.9
Viscose (bright)	>150	<0.3	>1.9
Viscose (matt)	>150	<0.3	>1.9
Tricel	>150	<0.3	>1.9
Celafibre	>150	<0.3	>1.9
Celafibre—acetone	>150	<0.3	>1.9
Celafibre—hydrolyzed	>150	<0.3	>1.9
Fibrolane	>150	<0.3	>1.9
Silk	>150	<0.3	>1.9
Terylene—NaOH	>150	<0.3	>1.9
Nylon	>150	<0.3	>1.9
Dynel	>150	<0.3	>1.9
Orlon	>150	<0.3	>1.9
Terylene	>150	<0.3	>1.9
Calcium alginate	>150	<0.3	>1.9
Ardil	>150	<0.3	>1.9
Thermovyl	>150	<0.3	>1.9
Courlene	110	1.5	0.7

favorable for individual paraffin molecules or clusters of molecules to be left in niches on the surface as the bulk liquid paraffin recedes. The adhesion of these individual molecules is favored by their substantial size.

Contact Angles in the Oil–Detergent Solution Systems

In Tables III to VI are given the results of contact angle measurements, calculated work of adhesion of the oil in the presence of detergent solution, and differences in adhesion energies in the following systems: liquid paraffin–0.01% Lissapol N, liquid paraffin–0.2% Lissapol N, olive oil–0.01% Lissapol N, and olive oil–0.05% Lissapol N.

It is seen from a comparison of the contact angles in the liquid paraffin–Lissapol N system with those in the liquid paraffin–water system that the effect of the addition of detergent to the water is, with the exception of calcium alginate, to increase the contact angle (in the oil) and to decrease the work of adhesion of the oil to the fiber. This effect is enhanced by increasing the concentration of the detergent, as can also be seen in the systems containing olive oil.

Fiber–Aqueous Interfacial Energy

The detergent influences the contact angle both by reducing the oil–water interfacial tension and by altering the fiber–water interfacial energy. Absolute values of the latter cannot be directly estimated from contact angle measurements, but differences between fiber–water interfacial energies in different systems can be deduced from the calculated values of adhesion energy differences in Tables II–VI. It is found that, in general, γ_{WF} is decreased by addition of detergent and by increasing concentration of detergent in the aqueous phase. A notable exception is calcium alginate. The change in γ_{WF} is indeterminate from these experiments for some of the systems because $\theta > 150°$.

TABLE V. Contact Angle, Work of Adhesion of the Oil to the Fiber, and Difference in Adhesion Energies in the System Olive Oil–0.01% Lissapol N

Fiber	Contact angle, °	Work of adhesion, ergs/cm.²	Difference in adhesion energies, ergs/cm.²
Celafibre	>150	<1.6	>0.11
Fibrolane	>150	<1.6	>0.11
Calcium alginate	125	5.4	7.2
Viscose (bright)	73	16.3	−3.7
Cotton	70	16.9	−4.3
Viscose (matt)	69	17.1	−4.5
Tricel	64	18.1	−5.5
Nylon	56	19.7	−7.1
Silk	50	20.7	−8.1
Thermovyl	45	21.5	−8.9
Orlon	35	22.6	−10.0
Courlene	34	22.6	−10.0
Dynel	33	23.2	−10.6
Ardil	<30	>23.6	<−11.0
Terylene	<30	>23.6	<−11.0

TABLE VI. Contact Angle, Work of Adhesion of the Oil to the Fiber, and Difference in Adhesion Energies in the System Olive Oil–0.05% Lissapol N

Fiber	Contact angle, °	Work of adhesion, ergs/cm.²	Difference in adhesion energies, ergs/cm.²
Cotton	>150	<0.8	>5.3
Viscose (bright)	>150	<0.8	>5.3
Viscose (matt)	>150	<0.8	>5.3
Celafibre	>150	<0.8	>5.3
Celafibre—acetone	>150	<0.8	>5.3
Celafibre—hydrolyzed	>150	<0.8	>5.3
Tricel	>150	<0.8	>5.3
Calcium alginate	>150	<0.8	>5.3
Fibrolane	>150	<0.8	>5.3
Silk	134	1.9	4.2
Nylon	125	2.6	3.5
Dynel	92	5.9	0.2
Thermovyl	83	6.8	−0.7
Orlon	81	7.1	−1.0
Terylene—NaOH	70	8.1	−2.1
Terylene	63	8.8	−2.7
Courlene	60	9.4	−3.1
Ardil	46	10.3	−4.2

The general pattern of these findings can be explained on the basis of the nonspecific adsorption of the detergent at the (relatively hydrophobic) fiber surface with the polar part of the molecule oriented towards the aqueous phase. On a hydrophilic surface there will be little or no such adsorption, as careful measurements have shown [5]. The adsorption phenomenon is, however, particularly with surfaces of intermediate polarity and heteropolar surfaces, complex, involving other factors such as electrostatic interaction and entropy changes, superimposed on the primary mechanism.

The increase in γ_{FW} for calcium alginate when 0.01% Lissapol N replaces water seems to be due to adsorption of the detergent with its hydrophilic head attached to the solid surface. Some of the reactions of polyethylene glycols [31] and the effect of anions on the surface activity of this type of compound [6] suggest that they have cationic character. Such a molecule would be readily adsorbed on the

TABLE VII. Residual Liquid Paraffin (%) on Fibers After Washing with 0.2% Sodium Oleate–0.1% Sodium Carbonate Solution at 39° and 49°

Fiber	39°	49°
Ardil	2	1
Nylon	6	8
Cotton	10	14
Terylene	62	47
Wool	88	89

TABLE VIII. Residual Olive Oil (%) After Washing with 0.2% Sodium Oleate–0.1% Sodium Carbonate Solution at 49°

Fiber	49°
Ardil	11
Nylon	2
Cotton	7
Terylene	60
Wool	10

negative sites of the alginate structure. γ_{FW} is decreased again in 0.05% Lissapol N solution. This suggests that a double adsorbed layer is formed at this detergent concentration. It is likely that the "reversed" type of adsorption occurs to a slight extent with other hydrophilic fibers, since they usually possess a small negative charge in water.

Fiber–Oil Interfacial Energy

The influence of the polarity of the oil on the oil–fiber interfacial energy can be seen by comparing the derived data for the olive oil–0.01% Lissapol N and liquid paraffin–0.01% Lissapol N systems. It is found that the oil–fiber interfacial energy is lower for olive oil than for liquid paraffin, and that the difference ($\gamma_{\text{liquid paraffin–fiber}} - \gamma_{\text{olive oil–fiber}}$) is pronounced except for Courlene and alginate. All the fibers, with the possible exception of Courlene, are more polar and possess higher surface energies than liquid paraffin; the fiber–oil interface, therefore, has an appreciable γ_{FO}. The more polar and polarizable olive oil is more capable of matching the surface free energy of the fibers, and γ_{FO} is, therefore, smaller.

On those fibers for which the difference in γ_{FO} can be determined, this difference is largest for Dynel, Ardil, and Orlon—the difference for Terylene is indeterminate but its lower limit is sufficiently high to indicate that this difference is the highest of all. This means that these fibers (relative to the other fibers) and particularly Terylene have a specific affinity for olive oil (relative to liquid paraffin). The finding

TABLE IX. Residual Liquid Paraffin (%) After Washing with 0.01% Lissapol N Solution at 22°C. and Corresponding Values of Residual Work of Detergency

Fiber	% Residual oil	Residual work of detergency, ergs/cm.²
Courlene	84	5.4
Alginate	69	0.23
Thermovyl	53	0.46
Orlon	51	0.13
Terylene	47	0.13
Terylene—NaOH	46	0.07
Silk	41	<0.05
Nylon	38	0.07
Viscose—matt	31	<0.05
Dynel	27	0.07
Viscose—bright	23	<0.05
Cotton	21	<0.05
Tricel	19	<0.05
Celafibre	18	<0.05
Celafibre—hydrolyzed	18	<0.05
Ardil	15	0.36
Fibrolane	9	<0.05

TABLE X. Residual Liquid Paraffin (%) After Washing with 0.2% Lissapol N Solution at 22°C. and Corresponding Values of Residual Work of Detergency

Fiber	% Residual oil	Residual work of detergency, ergs/cm.²
Terylene	26	<0.01
Nylon	7	<0.01
Cotton	5	<0.01
Ardil	3	<0.01

for Terylene is especially significant. The structures of both the fiber and the oil consist of ester groupings and paraffinic sections and the oil will presumably strive to present a surface at the Terylene surface which is similar to Terylene itself. It is conceivable that fatty nitriles and amides would similarly show specific adhesion to Orlon and nylon respectively. It is apparent that olive oil also has a low interfacial energy against Courlene. This derives presumably from the fact that the olive oil can be orientated to present a paraffinic surface at a like surface.

Detergency Evaluations

The results of the detergency experiments, expressed as percent residual oil (of original) on the fibers after washing, are given in Tables VII–XII. Results for the wool fiber[1] are included in Tables

[1] The detergency characteristics of wool are dealt with fully in the following paper.

VII and VIII. In the other tables, the calculated (from the contact angle) residual work of detergency [13] is included. This is the theoretical work required to change the contact angle of an oil droplet in the fiber from its equilibrium value to 180°, i.e., to complete displacement of the oil droplet. It is a more realistic measure of the difficulty of removing oil from a surface than is the work of adhesion, since it takes into account the change in shape of the oil droplets on removal.

The considerable variations in residual oil among the fibers confirm the important influence exerted by the nature of the textile in the detergency process.

TABLE XI. Residual Olive Oil (%) After Washing with 0.01% Lissapol N Solution at 22°C. and Corresponding Values of Residual Work of Detergency

Fiber	% Residual oil	Residual work of detergency, ergs/cm.²
Courlene	89	14.6
Terylene	87	>15.4
Dynel	86	14.8
Thermovyl	85	12.4
Alginate	81	9.4
Orlon	80	14.3
Nylon	60	10.3
Ardil	60	>15.4
Silk	41	11.3
Tricel	40	8.6
Cotton	28	7.3
Viscose—bright	24	6.8
Viscose—matt	22	7.6
Celafibre	22	<0.06
Fibrolane	10	<0.05

TABLE XII. Residual Olive Oil (%) After Washing with 0.05% Lissapol N Solution at 22°C. and Corresponding Values of Residual Work of Detergency

Fiber	% Residual oil	Residual work of detergency, ergs/cm.²
Thermovyl	52	2.5
Courlene	44	4.5
Alginate	43	<0.03
Terylene	41	4.2
Silk	33	0.21
Terylene—NaOH	28	3.5
Dynel	24	1.9
Tricel	17	<0.03
Orlon	14	2.7
Celafibre	12	<0.03
Ardil	11	5.8
Nylon	10	0.46
Cotton	8	<0.03
Viscose (bright)	8	<0.03
Celafibre—hydrolyzed	8	<0.03
Viscose (matt)	7	<0.03
Fibrolane	7	<0.03

This influence in these systems appears to be a quantitative one only, for examination of individual oiled fibers in the microscope showed that oil removal, when it occurred, always took place by "rolling up" and there was no evidence of other detergency effects such as, for example, complex formation.

In general, the ease of detergency of olive oil and liquid paraffin follows parallel patterns on the various fibers, but there are instances of "specific" adhesion. Thus, examination of Tables VII and VIII shows that the relative ease of detergency of olive oil and liquid paraffin is reversed when the substrate is changed from wool to Terylene. Terylene is also found to have a specific affinity for olive oil in the Lissapol N system. When Ardil and cotton are compared, olive oil is found to be relatively easier to remove from the latter. Dynel, relative to nylon and Orlon, is found to have a specific affinity for olive oil.

The detergency efficiencies of sodium oleate–sodium carbonate and of Lissapol N solutions also, in general, follow similar patterns on the various fibers, but there is an instance of "specific" interaction. Both olive oil and liquid paraffin are more readily removed from nylon than from cotton by the oleate–carbonate solution, while the reverse occurs with Lissapol N solution.

Correlation of Detergency Results with Oil–Detergent Solution Contact Angle Measurements

There is a general correlation of detergency results with contact angle measurements. There are, of course, many deviations, but the general trend of the residual oil values increases as the residual work of detergency increases. The implication of this is that Adam's theory of oil removal by rolling up, experimentally demonstrated for single fibers, is also an adequate basis for the description of the detergency process in assemblies of loose fibers.

It seems relevant to digress here and discuss the assertion of Lawrence [15] that phenomena involving interfacial energy are of minor importance in detergency and that the most important mechanism is that of penetration of the oil by the detergent and consequent complex growth formation. A thorough examination of the literature, however, shows that the rolling up mechanism is the more universal. The present investigation indicates that for nonpolar oils and moderately polar oils of the triglyceride type, interfacial energy effects are of primary importance;

it also seems that they have a considerable influence with the most polar oils, in which complex formation also takes place [8]. The mere fact of the important influence of the textile on the detergency process is in itself a denial of Lawrence's view.

The deviations from the detergency–contact angle relationship are, undoubtedly, due in part to the differing surface areas of the fibers per unit weight, as the detergency experiments have been carried out on equal weights of material; this is standard practice in detergency work. It is difficult to estimate and even to define the relevant surface areas. There being insufficient data available to use Kling's proposed method of deducing the required surface area [12], the detergency results were recalculated on the basis of the apparent geometrical surface areas, determined from projection microscope measurements. In Table XIII are shown the residual oil values of Table XII, converted to residual oil per constant area of fibers. The values for calcium alginate and Ardil are omitted and will be discussed separately later.

In this table it is seen that some of the discrepancies of Table XII have disappeared. Thus, silk is moved to a position more in accordance with its contact angle measurement, and Orlon and Tricel interchange positions. Minor deviations remain, as is to be expected in such a complex operation as detergency, where various factors affect the result. The most important of these will be the general alignment and elastic properties of the fibers, the influence of the fiber on redeposition, and the change in concentration of detergent arising from adsorption. Calculations, using adsorption data in the literature [30], suggest that 20% adsorption of 0.01% Lissapol N may occur on some fibers.

There are two anomalies—Ardil and calcium alginate—so outstanding that it is very unlikely that any or all of the above factors are solely responsible. With Ardil, the detergency is considerably better than contact angle measurements would suggest; with alginate, the reverse is so. The observation that both these fibers are especially weak and lack resilience when wet and, consequently, contract into a compact mass during the detergency operation, may be significant. The interfiber space must be relatively small; it is suggested that the detergency mechanism is, of necessity, the displacement of oil from capillaries. The detergency is controlled in such a situation not only by the advancing contact angle but by the hysteresis of contact angle and the geometry of the interfiber capillaries [17]. Hydrolyzed Celafibre behaves similarly (physically) to these fibers in aqueous solution and the same detergency mechanism may operate, but the result is compatible with the more usual rolling up process. The capillary displacement mechanism may operate to a slight extent with some other fiber systems and is another cause of deviations from the contact angle–detergency relationship.

TABLE XIII. Residual Oil Values from Table XII, Corrected for Relative Surface Areas of Fibers

Fiber	Residual oil (relative) per constant area, %	Residual work of detergency, ergs/cm.^{2}
Dynel	71	1.9
Courlene	69	4.5
Thermovyl	59	2.5
Terylene	42	4.2
Terylene—NaOH	29	3.5
Orlon	18	2.7
Tricel	14	<0.03
Celafibre	12	<0.03
Nylon	12	0.46
Silk	11	0.21
Viscose (bright)	10	<0.03
Viscose (matt)	9	<0.03
Fibrolane	9	<0.03
Cotton	8	<0.03

Limitation of Contact Angle Measurements

An aspect of the limitation of contact angle values for predicting detergency behavior is that better detergency is obtained with olive oil relative to the contact angle than is obtained with liquid paraffin. The main cause of this is probably differences in emulsion stability. It was experimentally confirmed that an emulsion of liquid paraffin in 0.01% Lissapol N solution was much less stable than one of olive oil. Similarly, the greater stability of an olive oil emulsion in 0.05% Lissapol N solution relative to 0.01% Lissapol N solution results in more efficient removal of olive oil in the former, relative to the contact angle value. The more efficient removal of the liquid paraffin (than of olive oil) in the dilute detergent solution, however, is an indication of the very marked influence of the fiber–liquid interfacial energies.

Detergency and Fiber Structure

In general, the ease of detergency increases as the polarity of the fiber increases. This conforms to the general principles of interfacial energy, for as the

fiber becomes more polar, the free energy of its interface with the oil becomes higher (so long as polarity of fiber > polarity of oil, as is usually the case in this investigation) while the free energy of its interface with the detergent solution tends to become lower.

The specific adhesion of oil to fiber, found in some instances in the detergency experiments, can also be explained on these principles. Thus, the relative difficulty of removing olive oil from Terylene and Dynel may be attributed to the low fiber–oil interfacial energy in these cases, due to matching of the polarity of the oil and the fiber.

A similar reason probably underlies the small degree of specificness of fiber–detergent solution interaction. Different detergents are likely to pack differently in their adsorbed layers at various surfaces, due to the interplay of such factors as electrostatic attraction, the entropy changes involved and the chemical structure, homogeneity, and roughness of the fiber surface. It should be possible to devise effective detergents for particular fibers by reducing the fiber–detergent solution interfacial energy to a minimum by matching the structure of the detergent to that of the fiber.

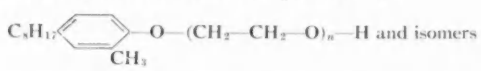
The extreme difficulty of removing oil effectively from a hydrocarbon fiber may be attributed to the detergent molecules being unable to pack on the fiber surface sufficiently well to produce an aqueous–fiber interface whose interfacial energy is about as low as that of the oil–fiber interface. There seem to be two possible methods of overcoming this difficulty. One is the use of a detergent with a fluorinated chain, in which the low inherent energy of the $-CF_2-$ and $-CF_3$ groups [23] should compensate for lack of condensed packing. The other is the use of two surface-active components in the detergent solution, capable of two-dimensional complex formation, thereby resulting in a closed-packed adsorbed layer at the fiber surface with a high proportion of $-CH_3$ groups in the interface. Soap alone, provided the concentration is such as to produce exactly the required amount of hydrolysis, is one example of such a system [8, 27].

Experimental

Materials

Sodium oleate—laboratory reagent standard.
Sodium carbonate—laboratory reagent standard.
Lissapol N—as supplied.

Chemical structure of sample used was



where n has average value of 9–10. Water content—3.6%.

Liquid paraffin—B.P.
Viscosity 788 sec. Red. I at 22° C.
Olive oil—laboratory reagent standard
Acid value 0.7 mg. KOH/g. oil
Viscosity 305 sec. Red. I at 22° C.
Textile fibers—These were exhaustively extracted with alcohol and with ether and conditioned at 22° C. and 67% RH.

Modification of Fibers

The surface layers of Terylene were removed by treatment with 10% aqueous sodium hydroxide at 95° C. for 5 min.

The acetyl groups of Celafibre were hydrolyzed by treatment with 2.5% sodium hydroxide solution containing 7% sodium chloride for 1 hr. at 20° C. [11].

The surface layers of Celafibre were removed by quick immersion in acetone.

Measurement of Contact Angle

The method used is similar in principle to that of Adam and Shute [2] and involves measuring the angle of inclination of the fiber to the liquid surface when the fiber (which passes through the surface) is tilted so that the liquid remains undisturbed on one side of the fiber. The apparatus devised for this work is shown diagrammatically in Figure 1. The

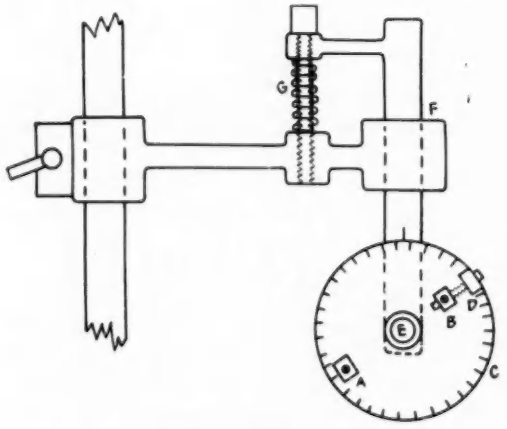


Fig. 1. Apparatus for the measurement of contact angles on fibers.

ends of the fiber being examined are attached to two blocks A and B. Each of these comprises two plates which are screwed firmly together when the fiber is in position between them. Block A is fixed to the disc C. Block B is mobile and is connected to another fixed block, D, by a screw. This screw is used to make the fiber (inserted loosely) just taut. The graduated disc, C, is mounted between rubber washers in such a way that it can be rotated smoothly. A hole, E, is bored through the disc and its supports so that the fiber can be illuminated from behind. Circles of cover-slip glass are glued on each end of this opening. Fine vertical movements of the apparatus can be made through the loose collar, F, by the screw and spring device, G.

The apparatus is lowered into an optical cell containing the liquid (or liquids) being examined. The cell is placed on a shelf attached to the stage of a travelling microscope.

Ideally, the center of rotation of the fiber should be exactly at the liquid interface. In practice, however, it was found more reliable to make a slight vertical movement of the liquid surface after each setting of the fiber inclination to ensure that the appropriate liquid was definitely advancing (or receding) as desired. The procedure for the measurement of, for example, the advancing angle of a liquid was as follows. An approximate value was first obtained, the fiber was set at this angle, and the liquid surface was moved up carefully into the field of view of the microscope. The meniscus at the fiber was observed for up to 10 min. (It was found that the meniscus curvature becomes practically constant in this period.) If, then, the liquid surface had not become flat right up to one side of the fiber, another setting of the latter, say 3–5° different, was adopted and the liquid surface raised slightly again to ensure the advancing state. Further positions of the fiber were observed, if necessary.

When working with oil–aqueous systems it was found that the contact angle depended on the length of time that the oil had been in contact with the fiber, but it was established that, if the contact time was ½ hr., there was no further appreciable dependence on time. In these experiments, the system was set up for ½ hr. before commencing observations, with the oil in contact with that part of the fiber on which the measurement was being made.

It was found possible to estimate the angles with a precision of ±3°. There are, however, other sources of error, such as the variation of the state of the fiber surface in some cases. Each measurement was made six times and the probable error is assessed at ±5° for measurements on water alone and at rather more for the liquid–liquid systems. In addition, there may be a constant "subjective bias." This technique demands more exercise of judgment than most physical observations and one observer's assessment of when the liquid surface is level right up to the fiber may be consistent yet differ from another's. The probable subjective bias could be of the order of 5–10°. That the results obtained are fairly reliable, however, is shown by their agreement with values obtained on the same materials by different techniques [4, 10].

All measurements were made at 22° ± 2° C.

Detergency Evaluations

The procedure was as follows. A bundle of purified fibers (2.5 g.) was soiled as uniformly as possible with 0.25 g. of oil, dissolved in ether. The ether was removed by a warm air current. The fibers were allowed to stand ½–1 hr. before washing.

A washing method was chosen in which the mechanical action was fairly gentle. Each sample of oiled fibers was placed on a steel perforated cage which was mechanically raised and lowered in a vessel containing 300 ml. of detergent solution (temperature control ±0.5° C.) for 15 min. The fibers were removed, squeezed gently, and rinsed twice in 300 ml. of distilled water. The amount of residual oil was obtained by extracting the oil from the fibers, evaporating the extract, and weighing the residue.

Each result is the mean of at least two values. The probable error varies from about ±2% for the lower range of residual oil values to about ±5% for the upper.

Interfacial Tension Measurements

The interfacial tension values required for some of the calculations were obtained by the Donnan drop pipette technique [20].

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The Removal of Oil from Wool and Its Relationship to Surface Structure

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Abstract

The difficulty of removing oils from undamaged wool is attributed to its possessing an epicuticle which is mainly paraffinic in nature. Various treatments are carried out on wool; it is shown that there are direct relationships among the polarity of the wool surface, the ease of oil removal, and the degree of completeness of the epicuticle. Treatments which render wool easy to wash are considered to do so by removing the hydrophobic epicuticle, thereby exposing the underlying hydrophilic keratin.

Introduction

There has not been general agreement on the relative difficulty of removal of oil from wool. Several authors [6, 28] have found that oil adheres to wool strongly relative to fibers in general, while recently Harker [8] has concluded that it is easiest to wash in a series of fibers including polyethylene, Terylene, nylon, and jute. Associated to some extent with this apparent anomaly is some uncertainty concerning the surface structure of wool. Thus, some authors assume that it is hydrophilic [8], while others consider that it is paraffinic [11]. It is widely held [5, 7, 19] that a thin membrane of different chemical structure from the bulk surrounds the fiber, while others [3, 6] attempt to interpret the surface prop-

erties of wool in terms of the bulk structure, i.e., polypeptide.

The purpose of this work is to achieve simultaneously some understanding of both of these aspects by examining the effect of modifications of the wool fiber on detergency and on the polarity of its surface. The Allwörden reaction is used to help to elucidate the nature of the modifications.

Results and Discussion

The Effect of Wool Type on Detergency

The ease of washing, on a basis of equal surface areas, of Devon long wool (36's), Lincoln wool (36's), and a New South Wales merino wool (66's) was compared. As seen from the results in Table I, the Devon and Lincoln wools were approximately equal in this respect and the New South Wales variety retained slightly more oil. These results indicate that wool probably does not vary appreciably in its detergency characteristics and, therefore, one type can be taken as representative—in this case, Lincoln wool.

TABLE I. The Residual Liquid Paraffin (%) on Three Types of Wool After Washing with 0.2% Lissapol N Solution at 22°C.

Wool type	Residual oil
Lincoln (36's)	57
Devon long wool (36's)	55
New South Wales merino (66's)	63

TABLE II. Contact Angle Between Water and Wool and Work of Adhesion of Water to Wool, the Wool Being Treated with Various Reagents

Treatment	Advancing angle, °	Receding angle, °	Work of adhesion, ergs/cm.²
Hypochlorite, pH 4	36	<30	131
$KMnO_4$/hypochlorite	36	<30	131
Acid hypochlorite	44	35	124
Sulfuryl chloride	46	38	122
KOH/alcohol	56	46	113
Permonosulfuric acid	71	69	96
Solid calcium hypochlorite	76	65	89
Boiling 2% sulfuric acid	76	74	89
Cold 16% hydrochloric acid	78	73	87
3 vols. hydrogen peroxide	91	84	72
Untreated	91	78	71
Silicone	107	105	51

Contact Angles Between Wool Fibers and Water

The advancing and receding contact angles for water on the variously treated wool fibers[1] were measured. The results are given in Table II, as are the corresponding calculated works of adhesion, based on the advancing angle. The work of adhesion is a measure of the strength of bonding of water to the wool surface and, therefore, of the polarity of the wool surface.

The salient features of these results are that the wettability of untreated wool is about the same as that of polyethylene (*cf.* preceding paper), that the various treatments result in a wide range of polarities of the wool surface, and that, in some cases, the wool is made about as hydrophilic as the cellulosic fibers (*cf.* preceding paper).

The Allwörden Reaction

These contact angle data are more significant when examined in conjunction with the results of the effect of chlorine water on the fibers (Allwörden reaction). Blisters are formed by this reagent on the surface of undamaged wool. The mechanism of this reaction has not been established with certainty but is generally held [2, 20] to be dependent on the fact that a fine membrane—the epicuticle—covers the wool fiber. It is considered that chlorine diffuses through the epicuticle and attacks the underlying layer. High molecular weight degradation products, which cannot diffuse through the epicuticle, are formed. The epicuticle thus acts as a semipermeable membrane and water flows in by osmotic pressure.

Information about wool modification can be obtained from examining either of two aspects of the Allwörden reaction[21]: the time of reaction and the extent to which it occurs. The latter was used in this investigation and can justifiably be regarded as a measure of the degree of completeness of the epicuticular sheath. The results for wool, which has been treated by various reagents, are given in Table III.

These results indicate that the epicuticle has been removed or perforated to various degrees by the different treatments. Thus the wool treated with hypochlorite behaves as if the epicuticle were completely destroyed; this occurs also to a considerable extent with the alcoholic potash treatment, less so with the permonosulfuric acid and sulfuryl chloride treatments, and only very slightly by the action of simple acids and hydrogen peroxide.

The action of alcoholic potash, deduced from these experiments, is contrary to the findings of Lindberg [15], but the time of treatment was shorter in

[1] Treatments described in experimental section.

TABLE III. Allwörden Reaction on Treated Wool: About 10 Fibers from Each Treatment Examined

Symbols: X = No reaction
R = Complete reaction; surface covered with blisters
Mod. = Moderate extent of reaction; surface partially covered
Sl. = Slight reaction; only a few blisters
V. Sl. = Very slight

Treatment	Results	Average
None	R R R R R R	R
H_2SO_4	R R R R R R R R R	R
HCl	Mod. R R Sl. R X R Mod. Sl.-Mod.	R
H_2O_2	R R R R Sl.-Mod. Mod. Mod. X R Mod.	R
Permonosulfuric	R Sl. R Sl. Sl.-Mod. Sl. Sl. V. Sl.	Mod.
Sulfuryl chloride	Mod. R V. Sl. R R R Mod. Mod. Sl. Mod. Sl.	Mod.
KOH/alcohol	X X X X V. Sl. X Sl.-Mod. Mod. X X	V. Sl.
Acid hypochlorite	X X X X X X	X
Hypochlorite pH 4	X X X X X X X	X
$KMnO_4$/hypochlorite	X X X X V. Sl. X X X X	X

his work. He accounts for the effect of this reagent on the surface properties of wool on the basis of a change in polarity of the epicuticle [16–18]. This seems to contradict his earlier work, in which he obtained membranes, presumably the epicuticle, in a badly damaged state by the action of alcoholic potash on wool [14]. Also, electron micrographs by Lagermalm and Philip [13] show some disintegration of the epicuticle, caused by alkali. Further convincing evidence that alkali causes removal or perforation of the epicuticle is that of Hock [10] who finds that the Allwörden bubbles on wool disappear on addition of alkali to the system.

Wikstrom et al. [29] have found that various reagents including alkali, perbenzoic acid, stannous chloride, *p*-benzoquinone, and sulfuryl chloride increase the wettability of wool. Extraction with solvents at fairly high temperatures had a similar effect. These authors claims that the effect of all these treatments can be explained on the basis of attack of the cystine bond of the keratin and that it is unnecessary to postulate the disintegration of an external layer. This argument does not deny, however, the possibility or even probability of the external layer being removed. La Fleur [12] attributes the increased wettability of wool by boiling water to the rupture of an external membrane.

Examination of the electron micrograph of a hypochlorite-treated wool shows that an external layer, in that case, is undoubtedly removed [24].

Nature of the Wool Surface

It seems that the paradox of the high regain and low wettability of wool is explained by the presence of an epicuticle whose chemical nature is different

TABLE IV. Contact Angles for Wool (Treated by Various Reagents) in the Liquid Paraffin–Water, Liquid Paraffin–0.01% Lissapol N, and Liquid Paraffin–0.2% Lissapol N Systems

Treatment	Contact angles, °		
	Liquid paraffin–water	Liquid paraffin–0.01% Lissapol N	Liquid paraffin–0.2% Lissapol N
Hypochlorite, pH 4	>150	>150	
Sulfuryl chloride	108	>150	
KOH/alcohol	79	>150	
Permonosulfuric acid	56	73	
Untreated	30	46	53
Silicone	30	<30	

from that of the bulk of the fiber. That pure wool is definitely nonwettable is shown by several workers [3, 11] as well as in this investigation. This cannot arise from surface roughness, the effect of which is to make the contact angle diverge from 90°. This conclusion is supported by the low degree of hysteresis of the wool–water contact angle. The nonwettability of the wool surface must, therefore, be due to its chemical nature, which must be largely paraffinic. This supports Elliot's suggestion that the epicuticle contains a waxy component [5].

Cassie [3] has recently attempted an explanation of the coexistence of the high regain for wool and its low wettability, assuming a keratin structure for the surface. He postulates that there is multimolecular adsorption of water vapor at the polar sites and considers that the contact angle is established by the influence of both the paraffinic sections and polar sites according to the equation $\cos \theta = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2$ where σ_1 and σ_2 are the proportions of

paraffin and polar surface and cos θ_1 and cos θ_2 are the cosines of the corresponding contact angles. The observed contact angle for wool could be obtained, however, only if σ_1 is much greater than σ_2, which is obviously not so for keratin. The ratio σ_1/σ_2 is larger for nylon and Terylene, and yet the wettability of these materials is greater than that of wool. Besides, other proteins have high wettabilities. The effect of some enzymes on wool at least requires the postulation of some non-protein components in the surface.

Friction measurements support the suggestion that the surface of wool has a paraffinic nature. Wool fibers are found to have a very low coefficient of friction (with scale), and it has been suggested that this is associated with the chemical inertness of the epicuticle [19].

Deductions about the surface structure of wool from zeta-potential measurements are suspect, since the experimental procedures used involve using ground wool or wool cut into short lengths, thereby exposing a considerable area of internal surface [9, 22, 25].

Correlation Between Wettability and the Allwörden Reaction in This Investigation

Examination of the contact angle measurements in relation to the results of the Allwörden reaction on the fibers shows that the wettability is directly related to the extent of degradation of the epicuticle. The sulfuryl chloride treatment is an exception. It is concluded that the wettability of the wool surface is influenced mainly by removal of the epicuticle, thereby exposing the underlying hydrophilic keratin. It is likely that as a secondary effect the different agents may result in different degrees of polarity of the exposed keratin and even occasionally of the epicuticle. It seems that the latter effect occurs with sulfuryl chloride treatment. Since the epicuticle is considered to be very thin—of the order of 100 Å—not much chemical attack can take place on it without rupturing it.

Contact Angles in Oil–Aqueous Systems

In Table IV are shown the contact angles (in the oil) in the liquid paraffin–water, liquid paraffin–0.01% Lissapol N, and liquid paraffin–0.2% Lissapol N systems. In Table V are shown those in the olive oil–0.01% Lissapol N and olive oil–0.05% Lissapol N systems.

It is seen that the more polar the fiber surface the greater the contact angle between that surface and the oil phase in these systems, as was also found for a miscellaneous set of fibers.[2] Also, the angles in the olive oil systems are lower than the corresponding ones in the liquid paraffin systems, arising from the fact that the polarity of olive oil is nearer generally to that of the fiber surfaces than is that of liquid paraffin.

TABLE V. Contact Angles for Wool (Treated by Various Reagents) in the Olive Oil–0.01% Lissapol N and Olive Oil–0.05% Lissapol N Systems

Treatment	Contact angles, °	
	Olive oil–0.01% Lissapol N	Olive oil–0.05% Lissapol N
Hypochlorite, pH 4	>150	>150
Sulfuryl chloride	70	150
Permonosulfuric acid	47	95
KOH/alcohol	30	90
Untreated	<30	56
Silicone	<30	<30

TABLE VI. Residual Oil (%) on Wool After Being Washed with Lissapol N at 22°C. and Corresponding Values of the Residual Work of Detergency

Oil	Conc. of Lissapol N, %	Residual oil, %	Residual work of detergency, ergs/cm.²
Olive oil	0.01	83	>15.4
Olive oil	0.05	24	4.9
Liquid paraffin	0.01	77	8.5
Liquid paraffin	0.2	57	1.8

Detergency Evaluations

The detergency results for untreated wool are given in Table VI. Those for modified wool in the olive oil–0.05% Lissapol N and liquid paraffin–0.2% Lissapol N systems are in Tables VII and VIII. In Tables VI and VII, the residual work of detergency [2] is also shown.

It is seen from Table VI that the degree of removal of olive oil and of liquid paraffin by 0.01% Lissapol N is of the same order, the residual olive oil being slightly higher probably as a result of its higher work of adhesion. The oil–fiber interfacial energy is low in both cases, since the wool surface is mainly paraffinic. At the higher level of detergent the olive oil is more effectively removed, presumably because it forms a much more stable emulsion.

In Table VII, the relationship (for, admittedly, only three fibers) between the residual oil and the

[2] Discussed in preceding paper.

residual work of detergency that has been found for fibers in general [2] is evident. The effect of the various treatments on the physical appearance of the wool fibers is usually negligible but sometimes results in a very slight accentuation of the scalar outline. The big differences in the degree of oil removal seen in Tables VII and VIII are, therefore, caused entirely by differences in the chemical structure of the surface.

The relationship between detergency and the polarity of the surface is further emphasized when the detergency data of Table VIII are compared in Table IX with the wettabilities (represented by work of adhesion of water) of the fibers and the results of the Allwörden reaction on the fibers.

The correlation among the residual oil, the work of adhesion of fibers to water, and the Allwörden reaction (except sulfuryl chloride) is striking. Those factors which complicate the surface structure—detergency relationship for a miscellaneous set of fibers are not so important here. Such are the surface areas, the adsorption of detergent, and the "structure" of the fiber assembly.

TABLE VII. Residual Olive Oil (%) on Wool (Treated by Various Reagents) After Being Washed with 0.05% Lissapol N at 22°C. and Corresponding Values of Residual Work of Detergency

Treatment	Residual oil, %	Residual work of detergency, ergs/cm.²
Untreated	24	4.9
KOH/alcohol	14	2.1
Sulfuryl chloride	3	0.03

TABLE VIII. Residual Liquid Paraffin (%) After Washing Wool (Treated with Various Reagents) with 0.2% Lissapol N at 22°C.

Treatment	Residual oil, %
Silicone*	73
Untreated	57
Hydrogen peroxide	55
Hydrochloric acid	42
Sulfuric acid	41
Calcium hypochlorite	32
Permonosulfuric acid	12
KOH/alcohol	4
$KMnO_4$/hypochlorite	2
Acid hypochlorite	1
Hypochlorite, pH 4	1
Sulfuryl chloride	1

* The silicone was extracted by the solvent, so correction had to be made.

It is concluded that the difficulty of washing oil from wool is due to its hydrophobic epicuticle, and that agents which render it easy to wash do so by disintegrating the epicuticle and exposing the underlying hydrophilic keratin. The epicuticle is a delicate membrane and is easily ruptured mechanically. Although it is undoubtedly protected on the fleece by wool wax, the different detergency results obtained for wool may be due in part to various degrees of breakdown of the epicuticle, possibly occurring during over-thorough purification procedures.

Experimental

Materials

The wool was washed thoroughly in cold water and extracted about 30 hr. each with alcohol and ether.

The other materials were the same as were used for the work described in the preceding paper.

Modification of Wool

Many of the reagents used in this work are known to affect the felting properties of the wool. In every case (except for *k*) the wool was rinsed thoroughly in distilled water after treatment.

a—Alcoholic potash [1]. Air-conditioned wool (6 g.) was treated with 150 ml. of a 2% solution of potassium hydroxide in 95% ethyl alcohol at 24° C. for ½ hr. It was rinsed in dilute hydrochloric acid.

b—Sulfuryl chloride [1]. Air-conditioned wool (6 g.) was treated with 150 ml. of a 2.5% (by vol.) solution of sulfuryl chloride in carbon tetrachloride

TABLE IX. Work of Adhesion (Fiber–Water), Residual Liquid Paraffin After Washing Fibers with 0.2% Lissapol N, and the Result of Allwörden Reaction on Variously Treated Wool Fibers

Treatment	Work of adhesion (water), ergs/cm.²	Residual oil, %	Allwörden reaction
Hypochlorite, pH 4	131	1	X
$KMnO_4$/hypochlorite	131	2	X
Acid hypochlorite	124	1	X
Sulfuryl chloride	122	1	Mod.
KOH/alcohol	113	4	V. Sl.
Permonosulfuric acid	96	12	Mod.
Calcium hypochlorite	89	32	
Sulfuric acid	89	41	R
Hydrochloric acid	87	42	R
Hydrogen peroxide	72	55	R
Untreated	71	57	R
Silicone	51	73	R

for 1 hr. at 22° C. It was rinsed in carbon tetrachloride.

c.—Acid hypochlorite [27]. A sample of wool (6 g.) was treated with 150 ml. of solution containing 0.14% available chlorine and 1% sulfuric acid for 15 min.; 3 ml. of sodium bisulfite was then added and the solution was stirred continuously for 5 min. The wool was then rinsed with distilled water and immersed in 150 ml. of 0.5 *N* ammonia.

d—Hypochlorite at pH 4 [4]. To 150 ml. of ice-cold water, including a trace of Teepol, was added sufficient sodium hypochlorite solution to produce 2% active chlorine, based on the weight of the wool. Formic acid was added until the pH reached 4. The temperature was adjusted to 5–10° C. and the solution volume to 180 ml. A sample of wool (6 g.) was added with brisk stirring, which was continued for 15 min. (The pH remained steady at 4.) Then, 6 ml. of 10% sodium bisulfite was added and stirring was continued for a further 10 min.

e—Potassium permanganate/hypochlorite [23]. A solution (300 ml.) was prepared containing 2.5% active chlorine, 1% potassium permanganate, 1% zinc sulfate, and 7% calcium chloride, these percentages being based on the amount of wool to be treated. The pH was 8.2. A sample of wool (6 g.), previously wetted with dilute Teepol solution, was immersed for 30 min. with gentle stirring in this solution. Then, 6 ml. of 10% sodium bisulfite and 6 ml. of 10% sulfuric acid were added. Stirring was continued until the brown color disappeared. The wool was neutralized as in *c*.

f—Permonosulfuric acid [26]. A solution of 1.5 ml. of 10% permonosulfuric acid in 180 ml. of water was prepared and the pH adjusted to 1.4 with sulfuric acid. Previously wetted wool (6 g.) was immersed in this solution for 1 hr. with occasional stirring. The wool was removed, squeezed, and immersed with stirring for 5 min. in 150 ml. of 0.2% sodium carbonate and then for 30 min. in 150 ml. of 2% sodium metabisulfite.

g—Sulfuric acid. A sample of wool (6 g.) was boiled with 150 ml. of 2% H_2SO_4 for ½ hr.

h—Hydrochloric acid. A sample of wool (6 g.) was immersed for 10 min. in 1 : 1 concentrated hydrochloric acid : water with occasional stirring.

i—Hydrogen peroxide. A sample of wool (6 g.) was treated with 300 ml. of 3 vol. hydrogen peroxide for 24 hr. (at pH 5.5).

j—Calcium hypochlorite. A sample of wool, conditioned at 22° C. and 67% RH, was immersed for 3 days in calcium hypochlorite powder. It was then washed in water and dilute acid.

k—Silicone. Zinc-2-ethyl hexoate, a curing agent, was incorporated (2% on wt. of wool) in the silicone reagent (Drisil 104). This reagent (5% based on wt. of wool) in ether solution was applied to the wool. The wool was then heated at 150° for 5 min. to "bake" the silicone.

Experimental Techniques

The experimental procedure for contact angle measurements and detergency evaluations are described in the preceding paper. For the Allwörden reaction, it was found most convenient to examine the fibers mounted on the contact angle apparatus and immersed in the cell containing chlorine water. The Allwörden blisters could be seen clearly through the microscope. The fibers were kept in the solution for 30 min. if necessary.

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Imparting Wrinkle Resistance to Cotton with 1,1′-Carbonylbisaziridine

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Abstract

Cotton print cloth and broadcloth were made wrinkle resistant by treating with carbonylbisaziridine (CBA) by the conventional process of padding, drying, and curing. Data are presented for fabric treated with and without the use of an acid catalyst, zinc fluoborate. An aftertreatment with Primenit VS emulsion [2] increased the crease recovery angle. Monsanto crease angles of over 300° were obtained with resin add-ons as low as 4.5%. In general the Elmendorf tearing strength was reduced 40–50%. This was improved somewhat by the use of a softener. The finish was quite stable to home laundering. When no catalyst was used in the solution, a reduction in breaking strength was observed after the chlorine bleach and scorch. When freshly prepared CBA solutions containing zinc fluoborate were used, there was no reduction in the strength of fabric after the chlorine bleach and scorch. However, all fabrics containing the finish were discolored in the scorched areas.

Introduction

There is a current interest in certain ethylenimine (or aziridine) derivatives as finishes for cotton brought about by research at the Southern Regional Research Laboratory. One of these new finishing agents, tris(1-aziridinyl)phosphine oxide, referred to as APO, has recently received attention as an excellent flame retardant when used in combination with tetrakis(hydroxymethyl)phosphonium chloride [6]. APO is also currently receiving attention as a potential wash-and-wear finish for cotton [5].

The purpose of this paper is to present data on a new resin-forming monomer, 1,1′-carbonylbisaziridine, referred to as CBA. CBA, like APO, is an ethylenimine derivative, and is made by the reaction of phosgene with ethylenimine, using an acid acceptor like triethylamine in an inert solvent such as benzene [4]. It may be represented by the formula

$$(NCH_2—CH_2)_2CO$$

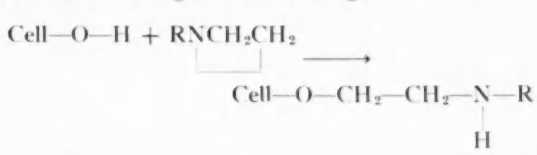
Work on CBA as a textile finishing agent was carried out simultaneously with the work on APO and is a segment of a broad program of research being

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Use of a company and/or product named by the Department of Agriculture does not imply approval or recommendation of the product to the exclusion of others which may be suitable.

undertaken to develop new or improved finishes for cotton fabrics.

CBA is a white crystalline hygroscopic compound having a melting point of 39–41°; it is soluble in water and many organic solvents. It is a very reactive compound, capable of forming a polymer and of reacting with cellulose. Current theory [2] is that the heterocyclic nitrogen reacts with an active hydrogen from a cellulose hydroxyl to split the ring and attach through an ether linkage.



Since CBA has two aziridinyl groups, it is capable of cross-linking the cellulose. It is also capable of forming hard insoluble cross-linked polymers. This is made possible by the formation of new reaction sites ($-\overset{H}{\underset{|}{N}}-$ groups) as the aziridine rings open up.

The process of treating cotton with CBA is a simple one, and can be done on standard resin-finishing equipment. It consists of impregnating the fabric with an aqueous solution of the monomer by immersion and removing the excess solution by passing the fabric through squeeze rolls. The fabric is then heated (with or without an added catalyst) to cross link the cellulose and at the same time to produce an insoluble cross-linked polymer inside the cotton fiber. The resulting fabric has good wrinkle resistance.

A serious drawback at present is the instability of CBA when stored at room temperature. This instability is due to the ease with which it polymerizes. However, it is stable for several months when stored in a refrigerator. The toxicity of CBA is not known, so due care should be used in handling it. When the curing process is carried out without an added catalyst, fumes are liberated which cause inflammation of the eyes if proper ventilation is not used. The presence of an acidic catalyst, such as zinc fluoborate, reduces the fumes during curing, thereby reducing the hazards. This is probably due to considerable prepolymerization.

Materials and Methods

The CBA used in these experiments was prepared in this laboratory from phosgene and ethylenimine essentially by the method used by Bestian [4], except the CBA was not distilled. The crude CBA as prepared was a liquid at room temperature and contained a viscous water-soluble polymer. This crude product crystallized when placed in a refrigerator. In some experiments the crude CBA was used; in others it was purified by filtration of the crystalline mass to separate the liquid polymer. In still other experiments CBA was prepared by a slightly modified technique in which the benzene and triethylamine were dried, the ethylenimine freshly distilled, and the reaction carried out in a nitrogen atmosphere. Also, a more complete removal of triethylamine hydrochloride was carried out. In this way a purer product was obtained than had been possible before.

Most of the experimental work was done with a desized, scoured, and bleached 80 × 80 cotton print cloth, 3.2 oz./sq. yd. One other fabric was used: combed cotton broadcloth, 140 × 60, singed, desized, peroxide bleached, and Sanforized.

In most cases the finishing agent was applied in the conventional manner of padding, drying, and curing in a forced-draft oven. A nonionic wetting agent was used in the aqueous treating solutions so as to obtain uniform and thorough penetration. Following the cure, the fabrics were washed thoroughly in hot water.

The concentration of CBA in the treating solutions was based on the total weight of the solution. In some of the experiments zinc fluoborate as a 40% solution was used as a catalyst. Catalyst concentration was based on the weight of CBA in the treating solution. Primenit VS (a 20% emulsion of N,N′-octadecylethylene urea) was used as a softening agent. The concentration of Primenit VS was based on the total weight of the treating solution.

Approximate resin add-ons were calculated from the air-equilibrated weight of the fabric after a process wash. A process wash consisted of rinsing for 30–60 min. in hot running tap water. The percent efficiency of resin formation within the fabric was calculated from the amount of CBA in the treating solution, the wet pickup of the fabric, and the resin add-on of the dry fabric after a process wash. The following equation was used:

$$\% \text{ Efficiency} = \frac{(\% \text{ add-on of resin})(100)^2}{(\% \text{ CBA in solution})(\% \text{ wet pickup})}$$

Fabric samples were washed with a synthetic de-

tergent in an agitator-type home automatic washing machine.

Textile tests were performed under controlled conditioning at 70° F. and 65% relative humidity, employing ASTM standard methods for the following tests: tearing strength by the Elmendorf Method [3a], crease recovery (warp and fill) by the Monsanto Method [1b], flex abrasion by the Stoll Method [3b], and strip breaking strength [3c]. Damage due to chlorine retention was tested by the AATCC Method [1a]. The wet crease recovery was carried out in the folowing manner. The samples were soaked for 5 min. at 65° C. in water containing a wetting agent and then blotted between two pieces of standard blotting paper. The crease recovery angles were then measured by the Monsanto Method. All crease angles reported are dry crease angles unless otherwise specified.

Experimental and Discussion

Influence of Crude CBA Concentration on Physical Properties

This experiment was carried out in order to establish the preferred concentration of crude CBA to obtain the best wrinkle resistance. Aqueous solutions of CBA were used containing 1% Triton X-100[2] as a wetting agent. The solutions contained 15, 20, 25, and 30% CBA. No added catalyst was used in this experiment. Samples of 80 × 80 print cloth were padded through the various solutions at a tight nip so that the wet pickup was approximately 70–75%. The samples were dried for 5 min. at 85° C. and cured for 5 min. at 150° C., then process washed and dried. Part of each sample was softened by padding through a 1% aqueous emulsion of Primenit VS and drying at 85° C. for 30 min. The efficiency, based on resin add-on, decreased with an increase in the concentration of CBA in the treating solution, as shown in Table I. A crease recovery angle of 246° was obtained on fabric treated with a 15% solution. This angle was not increased by increasing the concentration of CBA in the solution. There was a 50–55% loss in tearing strength which did not change significantly with solution concentration. There was approximately a 32–40% loss in breaking strength, the greater loss occurring with the higher concentrations. The use of the softener improved the wrinkle recovery by about 30°, increased the Elmendorf tearing strength by 12–18%, and decreased the breaking strength by 13–22%. The moisture content of the treated samples was about 2.5% less than that of the control.

Influence of Curing Time and Temperature on Physical Properties of 80 × 80 Print Cloth Treated with Crude CBA

For this study a 20% solution of CBA was used with 1% Triton X-100 as a wetting agent. Again no catalyst was employed. The same procedure as above was used in the treatment. The curing times were 5, 10, and 15 min. and the curing temperatures were 140° C. and 150° C. At a curing temperature of 140° C., only a slight increase in resin add-on was achieved by increasing the time from 5 to 15 min., as shown in Table II. At 150° C. no increase in resin add-on was obtained by increasing the time from 5 to 15 min. An approximately 15–20% increase in resin add-on was obtained by increasing the temperature from 140° C. to 150° C. The slight increase in wrinkle recovery angles accompanying the increase in time and temperature was not considered very significant. A curing time of 5 min.

TABLE I. The Influence of Crude CBA Concentration (Without Catalyst) Upon Physical Properties of 80 × 80 Print Cloth

CBA solids, %	pH of CBA solution	Resin add-on, %	Efficiency, %	Moisture content, %	Wrinkle recovery (W + F), degrees		Tearing strength (warp), g.		Breaking strength (warp), lb.	
					T	T + S	T	T + S	T	T + S
15	8.4	6.7	64	4.22	246	263	620	698	31.9	26.6
20	8.5	7.5	51	4.10	235	268	600	708	34.1	27.6
25	8.7	7.2	38	4.23	229	258	633	714	36.3	30.6
30	8.8	7.8	35	4.11	231	263	627	728	35.3	30.7
Untreated control				6.72	177	—	1304	—	53.6	—

T = treated with CBA; T + S = treated with CBA and softener (Primenit VS).

at 150° C. was considered to be about the best conditions for obtaining the best over-all properties. The softener improved the crease angles by approximately 25° and increased the Elmendorf tearing strength by 21–34%. The breaking strength was decreased by approximately 10–15% after softening. The control fabric in Table II was from a different roll of fabric than the one used in Table I.

Influence of Aging of Purified CBA Solutions on Physical Properties of Fabric

For this study the CBA was purified by filtering a slurry of the crude CBA to separate the pure crystalline compound from the liquid polymeric portion. The same procedure as above was used in applying a 15% aqueous solution of CBA to 80 × 80 print cloth. The solution had a pH of 8.2. The fabric was dried for 5 min. at 85° C. and cured for 5 min. at 150° C. Samples were treated after the solution was allowed to age at room temperature for ½, 5, and 24 hr. As shown in Table III, the resin add-on increased with the age of the solution. The efficiency of add-on when fresh 15% solutions of pure CBA were used was lower than that obtained when crude CBA was used. However, higher crease angles were obtained at lower resin add-on (and lower efficiency) when using pure CBA. The hand of the fabric was little affected after aging of the CBA solution for 5 hr. and was only slightly crisp after 24 hr. When CBA containing less initial polymer was used, a crease recovery angle of 281° was obtained on an unsoftened sample with only 4.5% resin add-on. This presumably is due to a higher degree of cross-linking of the cellulose with less resin formation. Elmendorf tearing strength was reduced about the same amount as when crude CBA was used (see Table II). The loss in breaking strength (37–49%) was considerably greater than when crude CBA was used. In general there was little change in fabric properties when using solutions ½ hr. or 5 hr. old. When 24-hr. old solutions were used there were generally slightly lower crease angles and higher tearing and breaking strengths. The effect of the softener was similar to that of

TABLE II. The Influence of Curing Time and Temperature on Physical Properties of 80 × 80 Print Cloth Treated with 20% Crude CBA (Without Catalyst)

Cure temp., °C.	Cure time, min.	Resin add-on, %	Efficiency, %	Wrinkle recovery (W + F), degrees		Tearing strength (warp), g.		Breaking strength (warp), lb.	
				T	T + S	T	T + S	T	T + S
140	5	6.1	39	242	265	580	748	39.1	34.7
140	10	6.5	42	250	277	572	742	40.1	34.9
140	15	6.8	44	252	277	532	712	37.2	32.7
150	5	7.1	46	253	278	560	680	39.7	33.8
150	10	7.1	46	258	278	528	684	39.3	32.2
150	15	7.2	47	258	278	532	676	38.0	32.5
Untreated control				159	—	1135	—	43.1	—

T = treated with CBA; T + S = treated with CBA and softener (Primenit VS).

TABLE III. The Influence That Aging of a 15% Purified CBA Solution (Without Catalyst) Has Upon Physical Properties of 80 × 80 Print Cloth

Age of solution, hr.	Resin add-on, %	Efficiency, %	Wrinkle recovery (W + F), degrees		Tearing strength (warp), g.		Breaking strength (warp), lb.	
			T	T + S	T	T + S	T	T + S
½	4.5	41	281	304	525	606	27.4	25.1
5	6.0	53	283	305	513	590	29.1	26.1
24	8.8	78	277	282	560	615	33.7	30.8
Control	—	—	177	—	1304	—	53.6	—

T = treated with CBA; T + S = treated with CBA and softener (Primenit VS).

samples shown in Table I; wrinkle recovery angles and tearing strength were increased and the breaking strength was decreased.

Influence of Aging of CBA-Treated Fabric on Crease Recovery

A sample of print cloth was padded with 20% aqueous solution of purifiel CBA, dried 5 min. at 85° C., cured 5 min. at 150° C., and softened with Primenit VS. The wrinkle recovery angle increased from 288° to 305° after the fabric had aged for one year. A second sample was treated first with a 10% solution of CBA and dried and cured like the first sample. Then the same sample was immediately treated again in the same way with a 5% solution of CBA. The wrinkle recovery angle increased from 293° to 317° after the treated fabric had aged for one year.

Influence of Primenit VS Aftertreatment Versus Primenit VS in Treating Bath

A sample of 80 × 80 print cloth was treated with CBA by the usual procedure and then softened by padding through a 1% emulsion of Primenit VS and drying for 30 min. at 85° C. A second sample was treated with CBA by the usual procedure except that the 1% Primenit VS was not applied as an aftertreatment but was placed in the treating solution. The aftertreatment gave the higher wrinkle recovery angle (272° vs. 259°), Elmendorf tearing strength (713 g. vs. 647 g., warp), and flex abrasion (424 vs. 281 cycles, warp).

Influence of Home Laundering on Physical Properties

The samples of fabric treated with purified CBA appearing in Table III were given 5 and 15 home launderings; then wrinkle recovery was measured. The results are shown in Table IV. All of the samples retained 90–100% of their crease recovery after either 5 or 15 home launderings. Crease recovery angles varied from 267 to 274° on the unsoftened samples and from 273 to 293° on the softened samples after 15 home launderings.

Wet and dry crease recovery, breaking strength, and tearing strength data before and after 15 home launderings are shown in Table V for additional samples of print cloth treated with purified CBA without a catalyst. After 15 home launderings the unsoftened sample retained 94% of its dry crease recovery and 96% of its wet crease recovery; it had an increase of 8% in tearing strength and 18% in breaking strength. The softened sample retained 92% of its dry crease recovery and 93% of its wet

TABLE IV. The Influence of Home Laundering on Crease Recovery of Print Cloth Treated with Purified CBA

Age of solution, hr.	Resin add-on, %	Wrinkle recovery (W + F), degrees: Before laundering T	Before laundering T + S	After 5 launderings T	After 5 launderings T + S	After 15 launderings T	After 15 launderings T + S
½	4.5	281	304	268	296	267	273
5	6.0	283	305	280	302	268	289
24	8.8	277	282	275	299	274	293
Control	—	177	—	197	—	—	—

T = treated with CBA; T + S = treated with CBA and softener (Primenit VS).

TABLE V. The Influence of Home Laundering on Physical Properties of Print Cloth Treated With Purified CBA (Without Catalyst)*

Type of treatment	Before laundering: Crease recovery (W + F), degrees: Wet	Before laundering: Crease recovery (W + F), degrees: Dry	Before laundering: Breaking strength (warp), lb.	Before laundering: Tearing strength (warp), g.	After 15 launderings: Crease recovery (W + F), degrees: Wet	After 15 launderings: Crease recovery (W + F), degrees: Dry	After 15 launderings: Breaking strength (warp), lb.	After 15 launderings: Tearing strength (warp), g.
Unsoftened	264	280	29.8	447	255	264	32.3	527
Softened	283	303	22.8	587	263	278	26.8	613

* These samples were about one year old at the time they were laundered and tested.

crease recovery; it had an increase of 17% in breaking strength and 4% in tearing strength. The softened sample shown in Table V was boiled for 3 hr. in a 0.5% soap solution containing 0.2% sodium carbonate. Before the boil the sample contained 1.21% nitrogen; after the boil it contained 1.15% nitrogen. This test showed very good stability of the resin finish to alkaline hydrolysis.

Zinc Fluoborate as a Catalyst

In preliminary experiments $Zn(BF_4)_2$ was used as a catalyst in the application of crude CBA to cotton fabric. The catalyst did not seem to be satisfactory when crude CBA was used; in fact, a slight yellow color was imparted to the fabric. However, when CBA of a higher purity was used the catalyst was more effective. The CBA used in the following study was prepared by the modified technique described under Materials and Methods. A series of experiments was carried out at CBA concentrations of 10% and 20% and catalyst concentration varying from 1% to 10%. The solutions were prepared by dissolving the CBA in water and then adding the catalyst prior to padding. After the padding operation the samples were dried for 5 min. at 85° C. and cured for 5 min. at 150° C. The pH was measured just before the application of the solutions to the fabric, which in all of the 20% solutions was within 5–10 min. after the addition of the catalyst. In all of the 10% solutions except the ones containing 8% and 10% catalyst, the catalyst was added 30–60 min. before padding. The pH of most of the solutions shown in Table VI varied from 6.2 to 7.0 Three solutions had pH values of 7.4, 7.6, and 7.7. These higher values were due to the fact that the solutions were 30, 45, and 60 min. old at the time the pH was measured. This increase of pH with the age of the solution was characteristic when $Zn(BF_4)_2$ was used as a catalyst. After 24 hr. the solutions reached a pH of about 8. The pH of the original solutions before addition of catalyst was about 8. The increase in pH is apparently due to the gradual opening of the ethylenimine ring structure in the presence of the catalyst. The results of the catalyst study are shown in Table VI. In general there was an increase in resin add-on with an increase in catalyst concentration. At a 20% CBA solution concentration the resin add-on varied from 3.0% with 1% catalyst to 14.6% with 10% catalyst. A resin add-on of 3% at a 1% catalyst concentration seemed abnormally low in this particular series, since under the same conditions a resin add-on of 6.1% was obtained without catalyst. The efficiency of resin add-on varied from about 40% with no catalyst to

TABLE VI. The Influence of Zinc Fluoborate Concentration on Properties of Print Cloth Treated with CBA*

CBA concentration, %	$Zn(BF_4)_2$ concentration, %	pH of CBA solution	Resin add-on, %	Efficiency, %	Crease recovery (W + F), degrees		Tearing strength (warp), g.	Breaking strength (warp), lb.	Elongation at break (warp), %	Breaking strength after chlorine bleach and scorch (warp), lb.
					Wet	Dry				
20	1	7.0	3.0	21	268	260	453	22.0	5.2	15.0
20	2	7.0	7.2	45	259	273	460	23.4	5.5	24.7
20	3	6.5	6.4	44	265	267	433	22.8	4.9	26.6
20	4	7.0	10.8	71	255	271	473	25.3	5.4	32.7
20	5	6.4	8.9	60	260	266	460	24.8	4.8	27.6
20	6	6.9	12.3	78	257	282	447	22.7	4.7	28.4
20	7	6.7	12.2	80	245	275	487	23.0	4.7	32.2
20	10	6.4	14.6	96	243	278	507	24.6	4.3	30.6
10	1	7.6	2.4	33	258	269	467	21.3	5.8	22.0
10	2	7.4	5.4	70	260	269	487	18.7	4.9	18.3
10	3	6.6	3.5	49	265	266	480	23.5	5.3	20.1
10	4	7.7	3.5	48	245	256	487	22.4	5.3	15.1
10	5	6.6	3.6	50	260	256	520	24.8	5.7	19.9
10	6	6.8	7.2	—	—	269	—	—	—	—
10	8	6.8	7.3	95	248	272	520	23.4	5.5	29.6
10	10	6.2	6.6	84	249	263	547	24.1	5.9	26.8
Control	—	—	—	—	177	197	1147	46.1	8.6	—

* No softener was used on the fabric samples in this experiment.

about 96% with 10% catalyst when using 20% solutions of CBA. At a 10% CBA solution concentration the resin add-on varied from 2.4% to 7.3% depending on the catalyst concentration. Efficiencies were as high as 95% at an 8% catalyst concentration. Wet crease recovery angles varied from 243° to 268°. It is interesting to note that the lowest wet crease recovery was obtained at the highest catalyst concentration and resin add-on, and highest wet crease recovery was obtained at the lowest catalyst concentration and resin add-on. Dry crease recovery angles varied from 256° to 282°. Good wet and dry crease angles were obtained at both low and high catalyst concentrations and resin add-ons. For example, a sample of fabric treated with a 20% CBA solution containing 3% catalyst had a resin add-on of 6.4%, a wet crease angle of 265°, and a dry crease angle of 267°. A sample treated with a 10% solution containing 3% catalyst had a resin add-on of only 3.5%, but had a wet crease angle of 265° and a dry angle of 266°. This would indicate that there is not much advantage in higher add-on as far as crease recovery is concerned. The warp tearing strength varied from 433 g. to 547 g. These values represented a strength loss of 52–62%. The use of softening agents would be expected to increase the tearing strength. The strip breaking strengths of the treated samples varied from 18.7 lb. to 25.3 lb. This represented a breaking strength loss of 45–60%. Breaking strength losses were significantly greater when zinc fluoborate was used as a catalyst. The elongation at break was 4.3–5.9% compared to the control at 8.6%.

Four samples were selected from Table VI and boiled for 3 hr. in a 0.5% soap solution containing 0.2% sodium carbonate. The crease recovery angles of these samples are shown in Table VII. There was a slight decrease in the wet crease recovery angles and a slight increase in the dry crease recovery angles. These differences were small and were probably within experimental error. It can probably be concluded that there was no significant change in the wet and dry crease angles after a 3-hr. soap-soda boil.

Damage Due to Chlorine Bleach

The samples of print cloth shown in Table V were treated with CBA without the use of a catalyst. Chlorine damage was determined on these samples before and after 15 home laundering cycles. It is evident from the breaking-strength losses that considerable damage resulted after the chlorine bleach and scorch. The unsoftened and softened samples retained only 46% and 50% strength before laundering. After 15 laundry cycles the strength retentions were 55% and 53%. It should be noted, however,

TABLE VII. The Influence of Soap Boil on Crease Recovery of Print Cloth Treated with CBA and $Zn(BF_4)_2$

CBA concentration, %	$Zn(BF_4)_2$ concentration, %	Resin add-on, %	Crease recovery (W + F), degrees: Before soap boil, Wet	Before soap boil, Dry	After soap boil, Wet	After soap boil, Dry
20	3	6.4	265	267	263	277
20	5	8.9	260	266	258	282
10	3	3.5	265	266	257	268
10	5	3.6	260	256	252	259

TABLE VIII. Properties of Broadcloth Treated With CBA and $Zn(BF_4)_2$

Treatment	Resin add-on, %	Efficiency, %	Crease recovery (W + F), degrees: Wet	Dry	Tearing strength (warp), g.	Breaking strength (warp), lb.	Elongation at break (warp), %	Breaking strength after chlorine bleach and scorch (warp), lb.
CBA	11.0	74	276	289	400	38.3	6.7	41.5
Control	—	—	—	194	932	74.5	13.9	—

that even though there was extensive chlorine damage, this damage was not increased due to laundering. All of the samples were discolored after the bleach and scorch test.

Data on chlorine damage of print cloth treated with CBA and zinc fluoborate are shown in Table VI. In every case where 20% CBA solutions were used but one, the breaking strength of the fabric samples showed an increase after the chlorine bleach and scorch. The one exception was the experiment in which 1% $Zn(BF_4)_2$ was used. The reason for an increase in strength is not known, but it is evident that cotton fabric treated immediately with freshly prepared solutions containing zinc fluoborate does not suffer the strength loss of fabric treated with solutions containing no catalyst. All of the 10% solutions shown in Table VI, except the ones containing 8% and 10% catalyst, were 30–60 min. old at the time they were applied to the fabric. The solutions containing 8% and 10% catalyst were applied to the fabrics within 5–10 min. after preparation. The breaking strength of fabric samples after a chlorine bleach and scorch was reduced in almost every case where the solutions were allowed to age for a while before treating the fabric. In the two cases where the freshly prepared solutions were used, the breaking strength increased after the chlorine bleach and scorch. This illustrates the importance of applying the solutions to the fabric immediately after their preparation. Even though the breaking strength of many of the samples was not reduced by the bleach and scorch, all of the samples were discolored in the scorched area.

Application of CBA to Broadcloth

A sample of broadcloth was treated with a 20% solution of CBA at a $Zn(BF_4)_2$ concentration of 7%. The treatment was carried out in the same manner as that described in the catalyst study shown above. The physical properties are shown in Table VIII. The sample had a wet crease angle of 276° and a dry crease angle of 289°. There was a tearing strength retention of 43% and a breaking strength retention of 51%. The elongation at break was 6.7%, compared to the control at 13.9%. The breaking strength retention after a chlorine bleach and scorch was 56%. This represented a slight increase over the breaking strength before chlorine bleaching. However, the sample was discolored in the scorched area in the same manner as described for print cloth.

Hand and Appearance

The hand of CBA-treated fabric is only slightly altered. It has a little fuller hand and is more resilient than untreated fabric. The wash-wear appearance was good after 15 home laundering cycles, followed by tumble drying.

Summary

Cotton fabrics with high crease resistance were obtained by processing with a new resin-forming monomer and cross-linking agent called carbonylbisaziridine (CBA). The fabrics were treated by padding through an aqueous solution of CBA with or without the use of a zinc fluoborate catalyst, then drying and curing at an elevated temperature. An insoluble resin is formed within the fiber, and it is also believed that cross-linking of the cellulose occurs by the formation of ether linkages.

The hand and appearance of fabric treated with CBA are good. The amount of resin necessary to impart crease resistance is comparable to that required for other crease-resistant finishes. In general the tearing and breaking strengths of fabrics treated without the use of a zinc fluoborate catalyst are also comparable to those obtained with most wrinkle-resistant finishes. The strength and color of treated fabrics are damaged by a chlorine bleach and scorch when no catalyst is used in the treatment. When zinc fluoborate is used as a catalyst and the solution applied to fabric immediately after the addition of the catalyst, no strength damage occurs due to a chlorine bleach and scorch. However, fabric discoloration is still obtained in the scorched area. The finish is very resistant to home laundering and boiling alkaline solutions.

Acknowledgments

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Blending Cottons Differing Widely in Maturity

Part II: Effect on the Physical Properties of a Sheeting Fabric (Type 128)

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Abstract

This investigation compares properties of a Type 128 sheeting woven with yarns spun from a blend of fibers differing widely in fiber fineness with comparable properties of a similar sheeting woven with yarns spun from a control cotton of the same average fineness. The data demonstrate that blending fine with coarse fibers in proportions of 60% to 40% does not detrimentally affect the important physical properties of grey, bleached, and bleached and dyed fabrics. Commercial acceptability evaluations showed that, in general, marketable bleached materials can be manufactured from a blend of extremely fine and coarse fibers. The dyed fabrics were not generally commercially acceptable due to nep imperfections. These findings, which showed that cotton fibers differing extremely in fineness can be utilized successfully when blended properly, revealed that the generally accepted opinion of unsatisfactory processing performance of blends containing fibers of widely different finenesses may be due to the inadequacy of present blending systems and methods rather than the properties of the fibers.

Introduction

In a previous report [4] the effect of blends of cottons differing in fineness on the properties of single yarns was discussed. Yarns are utilized mostly in the form of woven or knitted materials, so their effect on the properties of finished fabrics is important. Information of this type is pertinent, since it is known that immature cotton dyes a different shade than mature cotton [5] and that, although fiber length and fineness influence neppiness, the proportion and distribution of thin-walled (immature) fibers contribute more to fabric defects than do either of these other fiber properties [11].

The first phase of this investigation [4] showed that single yarns of good quality can be produced from blends of fine and coarse cottons in proportions of 60% to 40%, provided an efficient blending technique is used. This report compares the physical and comercial acceptability properties of a Type 128 sheeting woven with the yarns spun from the blend of fine and coarse fibers and also with yarns spun from an unmixed cotton sample of about the same average fineness.

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Materials and Methods

Samples

The physical properties of the cottons and yarns used in this study have already been reported in Part I of this series [4]. Briefly, cottons having essentially equal fiber properties, except fiber fineness, were used. A blend was made of 60% of a fine (3.0 Micronaire reading) and 40% of a coarse (6.0 Micronaire reading) cotton, resulting in an average Micronaire reading of 4.0. For purposes of

TABLE I. Commercial Finishing Procedure

Finishing operations

Desizing	Scouring	Bleaching	Dyeing
3% Acid solution	3.5% Solution–NaOH	5% 35 vol. H_2O_2	2% Vat
(50/50 HCl and H_2SO_4)	0.5% Solution–detergent	2.5% sodium silicate	(on wt. of fabric)
80° F.	212° F.	180° F.	110–120° F.
1 hr. in J-box	1 hr. in J-box	1 hr. in J-box	Continuous

comparison a control cotton with a Micronaire reading of 4.0 was used. These cottons were then spun into appropriate yarn numbers for this study.

In general, fineness (estimated from air porosity measurements) and maturity are highly correlated in American Upland cottons, so that low Micronaire readings are usually associated with "immaturity." Therefore, the cottons referred to as "fine" and "coarse" in this report can also be considered as immature and mature, respectively. Also, fiber fineness as used in this paper can be interpreted in terms of either Micronaire readings, weight fineness (Suter-Webb) or specific area (Arealometer).

Processing Procedure

These cottons were processed into warp [21/1 (28 Tex) 4.5 T.M.] and filling [23/1 (26 Tex) 3.6 T.M.] yarns, which in turn were woven into a Type 128 sheeting of the following specifications:

Width	36 in.
Ends/in.	64
Picks/in.	64
Warp	21/1
Filling	23/1
Oz./sq. yd.	4.57

The fabric was woven 36 in. wide on a Draper XP 42-in. loom;[2] the evaluations made should apply to wider fabrics of this same construction. Four combinations of yarns were used in the fabric to determine how the blended cotton could be used most advantageously: control yarns in both warp and filling, C_wC_f; blended yarns in both warp and filling, B_wB_f; control yarns in the warp and blended yarns in the filling, C_wB_f; and blended yarns in the warp and control yarns in the filling, B_wC_f. Throughout this paper these identifying designations are used.

The fabrics were bleached or bleached and dyed on commercial equipment using the procedures [2] outlined in Table I. The shade chosen (vat Willow Green) is known to accentuate any defects in the fabrics.

Testing Procedures

Breaking strength and elongation-at-break were determined by the grab and strip (1-in.) methods [1a], using a constant-rate-of-traverse (pendulum) type tester. Tearing resistance was determined by the Elmendorf[2] method [1b] and also by the tongue method using the Instron[2] tester and Integrator. For the latter, a 3-in. tear in the fabric was integrated, while the Instron was operated at a crosshead speed of 12 in./min. Crimp was determined by the load elongation method using an IP-2 tester [1d]. Abrasion was determined by the flexing and abrasion method [1c]. The structural characteristics of the fabrics, including weight, thread count, and thickness, were determined in accordance with ASTM procedure [1a].

The differential dye test [3, 5], which distinguishes between fine (immature) and coarse (mature) fibers in terms of relative greenness or redness, was used to determine qualitatively the effectiveness of blending for raw stock, picker lap, drawing sliver, roving, yarns, and fabrics. Also, since fine cotton is known to nep more than coarse cotton, the effectiveness of the blend was judged by visual appraisal of the relative number of neps on the surface of the fabrics.

Comparative changes and variations in color between the blend (B_wB_f) and control (C_wC_f) fabrics were evaluated quantitatively by measurements of reflectance to magnesium oxide with a General Electric Spectrophotometer.[2] Tristimulus values based on the 1931 CIE standard observer and Illuminant C were obtained by use of a manual type integrator. Chromaticity coordinates were computed [9] and the colorimetric data reduced to Munsell renotations for hue, value, and chroma by means of tables and charts developed by Newhall, Nickerson, and Judd [10].

The market value of the fabrics was evaluated by an industry group, representing manufacturers of high quality sheeting materials.

[2] The mention of trade names does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

TABLE II. Effect of Blending Cottons Differing in Fineness on Weight and Thread Count of Grey, Bleached, and Bleached and Dyed Fabrics

Samples	Grey			Bleached			Bleached and dyed		
	Weight, oz./yd.²	Thread count		Weight, oz./yd.²	Thread count		Weight, oz./yd.²	Thread count	
		Warp	Filling		Warp	Filling		Warp	Filling
Control (C_wC_f)	4.79	65	64	4.42	79	57	4.46	80	57
Combination (C_wB_f)	4.83	65	64	4.42	79	56	4.52	81	57
Combination (B_wC_f)	4.97	65	65	4.42	78	58	4.62	80	59
Blend (B_wB_f)	5.05	65	64	4.46	78	59	4.50	80	58

Statistical analysis for significance of differences between means of breaking strength (grab and strip methods) was based on measurements made at the beginning and end of each fabric, with these locations being used as replications for measuring the significance of differences.

Discussion of Results

The following performance properties were used as bases of comparison for the fabrics made up of four different combinations of yarns: the two most important comparisons of the control (C_wC_f) versus the blend (B_wB_f) and two intermediate combinations (C_wB_f) and (B_wC_f).

a. Breaking strength, grab and strip methods
b. Breaking elongation, grab and strip methods
c. Tear strength, tongue and Elmendorf methods
d. Abrasion resistance, flex method
e. Crimp
f. Differential dyeing properties of yarns and fabrics
g. Bleaching and dyeing properties of fabrics
h. Commercial acceptability quality evaluations

Thread Count and Weight

Table II shows thread count and weight data of grey, bleached, and bleached and dyed fabrics. The finishing operations increased the thread count warpwise and decreased it fillingwise about the same percentage for all of the yarn combinations used in the fabrics. Fabric weight was about equal for all finished fabrics. Therefore, no significant constructional changes occur when a cotton mix contains fibers differing extremely in fineness.

Breaking Strength and Elongation Properties

Figure 1 shows grab breaking strength data for grey, bleached, and bleached and dyed fabrics. In the grey fabrics the warp strength was about equal

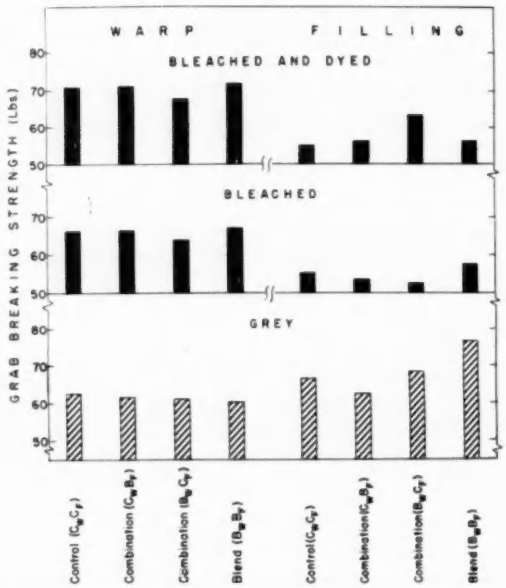

Fig. 1. Effect of blending cottons differing in fineness on the grab breaking strength of grey, bleached, and bleached and dyed fabrics.

for all combinations of fabrics whereas the filling strength for the blend fabric (B_wB_f) was greater than that of the control (C_wC_f). Generally, with the exception of one combination (C_wB_f), all of the grey fabrics had greater filling than warp strength. For the finished fabrics, warp as well as filling strengths were about equal for the four fabric combinations; however, in contrast to the grey fabrics, all of the filling strengths were lower than the warp strengths.

When evaluated statistically at the 95 or 99% probability levels, strength differences between means for the control (C_wC_f) and blended (B_wB_f) fabrics, warp and fillingwise for all the finished fabrics, were insignificant, as were the differences in means for the warp for the grey fabrics. Differences between

means of the control and blend fabrics for filling were significant at the 95% probability level. The significant difference between the mean filling strength of the blended filling yarn in B_wB_f and C_wB_f at the 95% level is quite evident. However, data on the physical properties of the C_wB_f and B_wC_f fabrics were obtained on samples of such limitations as to make meaningless any statistical comparison of physical properties with those of the C_wC_f and B_wB_f fabrics.

The effect of blending cottons differing in fineness on the grab breaking elongation of grey, bleached, and bleached and dyed fabrics is shown in Figure 2. With all fabric combinations, warp and filling, no differences in breaking elongation properties occurred. The greater filling breaking elongation of the finished over the grey fabrics resulted from crimp interchange during the commercial finishing operations.

Data shown in Figures 1 and 2, based on the grab test method, should be of immediate interest to the textile manufacturers, since they commonly use this method to obtain fabric strength data. Not shown are similar data obtained from the strip method of measuring fabric strength, which for all practical purposes corroborated observations made from data obtained from the grab method. Strength values obtained by this method were lower than grab strength values, due to the lack of fabric assistance. Corroboration of results obtained from the grab and strip method is particularly significant, since the latter method reflects more directly the influence of fiber properties. This proves that the presence of extremely fine and coarse fibers in a cotton blend will not detrimentally affect either the strength or elongation of a Type 128 sheeting.

Tearing Strength Properties

The data plotted in Figure 3 show the effects of blending cottons differing in fineness on Elmendorf tearing strength.

The data indicate only small differences in tearing strength among the four fabric combinations for both the grey and finished materials in the warp and filling directions.

When evaluated statistically, the warp tearing strengths of the bleached and dyed materials were significantly lower for the blended (B_wB_f) than the control (C_wC_f) fabrics; all other tearing strength differences, warp and fillingwise, were not significantly different.

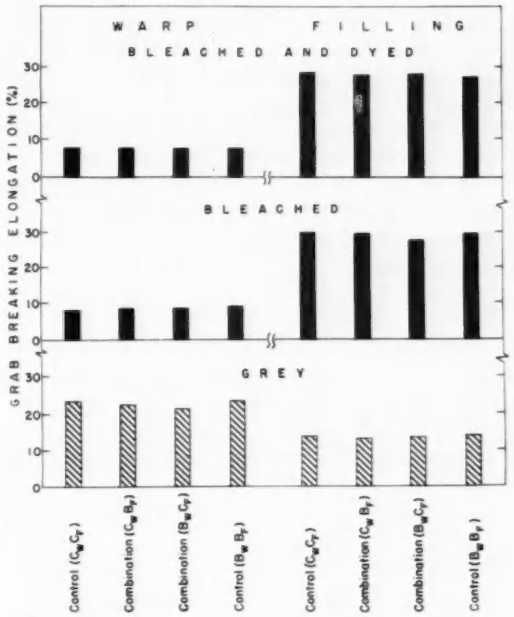

Fig. 2. Effect of blending cottons differing in fineness on the grab breaking elongation of grey, bleached, and bleached and dyed fabrics.

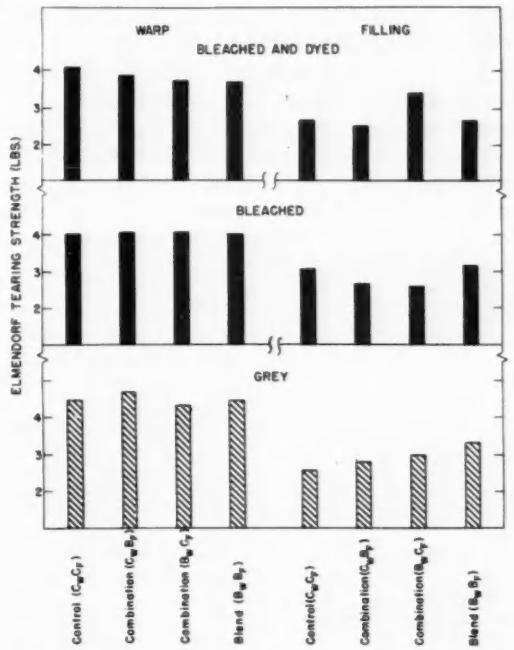

Fig. 3. Effect of blending cottons differing in fineness on Elmendorf tearing strength of grey, bleached, and bleached and dyed fabrics.

Tearing strength is an important fabric property and can be measured by various methods [12]. To obtain additional information on this important fabric property all fabric combinations were also subjected to the tongue tearing test. These data, not shown, corroborated those obtained using the Elmendorf technique. It can be concluded, therefore, that the tearing strength of a sheeting fabric is not affected when produced from blends of extremely fine and coarse fibers.

Abrasion Resistance

The control (C_wC_f) and blend (B_wB_f) fabrics showed no differences in resistance to abrasion in the grey or finished states. Abrasion resistance was less for the finished than the grey fabrics, but the rate of change was about the same for all fabric combinations. No important trends were apparent, so the data are not shown.

Crimp Properties

It was shown that yarn diameter influences crimp of grey and finished fabrics [8]. It is not too well known how yarns composed of blended fibers differing in fineness react to crimp during the stress of commercial finishing operations when considerable tension is generally applied, particularly in the warp direction. Figure 4 shows crimp values for the four combinations of fabrics. No differences in crimp existed between the control (C_wC_f) and blend (B_wB_f) fabrics. The dominant contributing variable influencing yarn crimp in a fabric apparently is the average fineness of a cotton mix [8] rather than the range in fineness in component fiber length groups of a cotton fiber population.

Differential Dye Properties

For grey fabrics, the differentially dyed blend (B_wB_f) appeared greener in shade than the control (C_wC_f), which had a reddish cast, but the uniformity of dyeing was about equal for both fabrics. This visual examination might indicate that the fine and coarse fibers in the blend (B_wB_f) were interspersed about as randomly and homogeneously as were the fibers in the control (C_wC_f).

For bleached fabrics, color shade differences between control (C_wC_f) and blended (B_wB_f) fabrics completely disappeared, implying that when dyed the resultant shades should be about similar. Only small modifications in dyeing procedure should be required to bring the shade of the blended fabric up to that of the control.

The fine and coarse cottons could be readily distinguishable in the picker lap form by their characteristic green and red shades. By the time yarns were produced, however, these fibers had been mixed homogeneously enough to make differentiation from the control yarns somewhat difficult—based on uniformity of dyeing, not differences in over-all shade.

Color Evaluations

To obtain quantitative differences in the bleaching and dyeing properties of the control (C_wC_f) and blend (B_wB_f) fabrics, the fabrics were dyed a Willow Green; spectral reflectance measurements were made and colors expressed in terms of Munsell renotation for hue, value, and chroma.

In the Munsell system the "value" is a measure of "brightness." The higher the value the brighter the sample, and this property is a highly desirable

TABLE III. Means and Measures of Variability for Colorimetric Data (Munsell Renotations) for Bleached and Bleached and Dyed Fabrics Woven from Cottons Differing in Fineness

	Bleached		Bleached and dyed					
	Value		Hue		Value		Chroma	
	Control (C_wC_f)	Blend (B_wB_f)	Control (C_wC_f)	Blend (B_wB_f)	Control (C_wC_f)	Blend (B_wB_f)	Control (C_wC_f)	Blend (B_wB_f)
Mean	9.337	9.343	1.180G	2.388G	4.606	4.778	1.678	1.745
Standard deviation	.016	.032	.708	.968	.052	.044	.133	.212
Coefficient of variation	.168	.342	60.0	40.5	1.13	.92	7.9	12.2
Standard error	.005	.010	.22	.31	.016	.014	.042	.067
Least significant difference,								
$P = 0.05$	.024		.796		.045		.166	
$P = 0.01$	.032		1.092		.062		.228	
Difference in means	.006		1.208*		.172*		.067	

* Highly significant.

quality in fabrics. The data in Table III show that, for both the bleached and bleached and dyed fabrics, the blend (B_wB_f) fabric is brighter than the control (C_wC_f), since the Munsell value is higher. When analyzed statistically, the difference between the mean value for the control and for the blend fabric was highly significant in the bleached and dyed fabrics but not in the bleached fabrics. For the bleached fabrics, the coefficients of variation indicate that the blend is more variable than the control fabric; for the bleached and dyed fabrics the reverse is generally indicated.

Low chroma indicates that the fabric tends to be more grey, i.e., departs from a pure hue. The data show that the chroma in the blended fabric is higher than in the control, although the difference is not statistically significant. However, the higher coefficients of variation for the blend again indicate that the blend is more variable than the control and presumably more "spotty." The control will appear more greyish to the eye. From a practical standpoint, to bring the chroma of the blend to that of the control, additional grey will have to be used.

The hue of all the dyed samples (control and blend) can be described as Green (G) in the Munsell system in this particular analysis, except one observation on a control which was Green/Yellow (GY). Within this one classification of green the mean for the blend was significantly higher than the mean for the control; in other words, the control is positioned in the direction of Green Yellow. Also, the

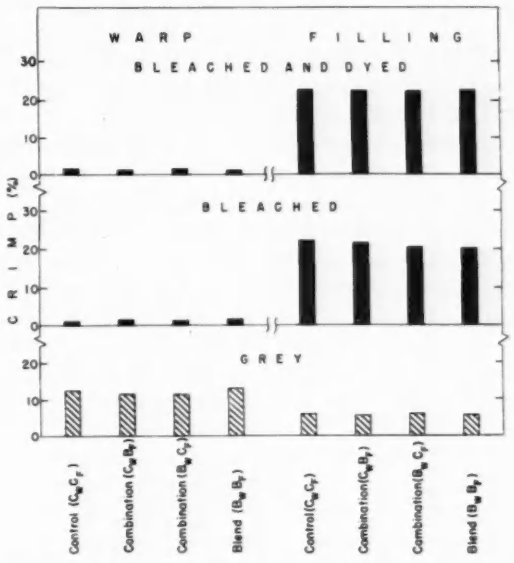

Fig. 4. Effect of blending cottons differing in fineness on the crimp of grey, bleached, and bleached and dyed fabrics.

TABLE IV. Commercial Acceptability Evaluations of Grey, Bleached, and Bleached and Dyed Fabrics Produced by Blending Cottons Differing in Fineness

Mill	Evaluations
A	The white bleached materials were considered commercially acceptable. The dyed fabrics made from the blend (B_wB_f) would be subject to complaints, mostly due to nep imperfections. A difference in shade between control and blended fabrics would involve use of more dye to dye the latter fabric to the same shade as the former.
B	The control is satisfactory but the combination fabrics (C_wB_f) and (B_wC_f) are "borderline," based on their appearance standards. The bleached blended fabric would not be commercially acceptable. All fabrics, both grey and finished, met strength standards.
C	There was no significant difference in market quality acceptance properties among the bleached fabrics of any four fabric combinations. However, for the bleached and dyed fabrics the control fabric was rated as being significantly better than the blended fabric. In general, however, any of the samples would constitute a commercially acceptable delivery.
D	All four fabric combinations were considered generally acceptable on the market, but the blended fabric contained considerably more neps and appeared more uneven than the fabrics made from the control. The combination fabric (C_wB_f) showed no improvement in quality, but the combination (B_wC_f) showed fewer neps and less unevenness with over-all quality approaching the control fabric.
E	There was little difference in any of the four fabric combinations in the bleached fabrics, with the blend being equal in appearance to the control. After being dyed, the former was inferior to the latter fabric in appearance due to more neps and slightly streakier dyeing.
F	Quality differences among the four fabric combinations were of a magnitude usually found among different shipments from the same cotton mix, or from the beginning and end of a season; or from one year to another.

blend is less variable than the control. This difference in hue could conceivably be corrected by adding yellow, but the amount to be added is so small that only the dyer will be in a position to decide this.

Commercial Acceptability Quality Evaluations

Grey, bleached, and bleached and dyed fabrics for the four fabric combinations were subjectively appraised for their quality acceptance on the market by a group of representatives connected with manufacturers of sheeting material. Rankings are based on the quality standards of each individual manufacturer, so the results are discussed on an individual, rather than group, basis. Table IV summarizes results of this evaluation.

From an over-all quality standpoint it appears that fine and coarse fibers can be blended to produce commercially bleached fabrics acceptable for most trade purposes. The increased number of neps present in dyed fabrics made from the blend (B_wB_f) tends to restrict the percent of fine fibers used as a component part of a blend designated for dyeing purposes; however, there is evidence that use of the fabrics with different combinations of warp and filling, (C_wB_f) or (B_wC_f), may provide opportunity to produce an acceptable dyed material.

Practical Applications

In interpreting results from this investigation, one should remember that the everyday merchandising of cotton fabrics is not based on any rigid commercial quality formula or uniform system of grading cloth quality acceptable to both vendee and vendor. In most cases acceptance quality provisions are arbitrarily established on an individual basis. Since the commercial acceptance evaluations were made by producers of top quality sheetings, these results are meaningful since they apply to the entire market quality acceptance range—with the greatest advantages being realized with the sheetings in the lower range of quality.

The results obtained in this investigation show that extremely fine and coarse fibers can in most instances be tolerated in bleached materials, and to a limited extent in dyed materials. It is significant that the major objections to the dyed fabrics from the blended fabric series was excessive "neppiness" rather than "streakiness." This means that the fine and coarse fibers are interspersed randomly enough not to cause such common defects as filling bars, streaks, etc. This observation is particularly important, since the shade of the dye used, Willow Green, is known to accentuate rather than mask imperfections. It may be possible, through a slight reduction in percentage of immature fibers in the blend, different types of dyes, darker shades, and modified finishing techniques such as the inclusion of mercerization prior to dyeing and/or bleaching, to minimize the imperfections noted to such an extent as to produce an acceptable dyed fabric.

There was some evidence that the quality of the combination fabric (B_wC_f) was better than the blend fabric (B_wB_f). This observation presents an opportunity to tailor cotton mixes to meet the end-use functional requirement of individual mills; i.e., if a blend of fine and coarse fibers used as both warp and filling yarns fails to meet market quality requirements of either bleached or dyed materials, the same blend used only as warp yarns may be satisfactory. For instance, with some fabrics, especially double-and-twist denims, the effects of dyeing are very critical in the filling because of the light shades required, whether the shade is obtained by dyeing all of the raw stock or by blending dyed raw stock with undyed white cotton in appropriate proportions. The available fine cotton then should not be used in the filling yarns but could probably be used in the mix for the warp, since it has been reported [13] that with the heavy indigo shades used in denim only an extremely fine (immature) cotton will show up in dyeing. Apparently then, once the fine fibers are properly interspersed in a cotton mix averaging about 4.0 Micronaire reading in the warp, no serious dyeing difficulties for denim should be experienced. Because of organizational machine "balancing" problems, availability of cotton qualities, and individual levels of market quality requirements, each manufacturer will have to work out his own suitable combinations of fine and coarse fiber percentages in the cotton mix and appropriate warp and filling yarn combinations in the fabric.

Although only one type of blend was used in this study—about a 1:1 proportion of cottons differing extremely in fineness—to produce a fabric of acceptable "average" commercial quality, the findings illustrate many practical ways in which fine cotton can be utilized. For example, if the average fineness of a cotton mix is too high (usually above 4.5 Micronaire reading), addition of about 10–20% of a 3–3.5 Micronaire-reading cotton will reduce the

average sufficiently to improve processing performance without sacrificing seriously any appearance or physical property requirements of the product being produced. In fact, increases in yarn strength would result. In cases where a mill has on hand large amounts of both the fine and coarse cottons, there is no reason to believe that performance or quality will be impaired if small amounts (up to about 20%) of each of these qualities are blended with the standard cotton (usually about 4.2 Micronaire reading) being used in everyday mixing stocks. The secret in this case is to be sure that the *average* fineness of an already good performing mix is neither reduced nor increased when blending the fine and coarse fibers into the cotton mix. A technique for calculating the proper level of fineness to use to obtain a specified average fineness of a cotton mix has already been developed [7].

These promising results are in all probability attributable to the blending technique, which was deliberately planned to insure maximum homogeneity. The fabrics produced in this experiment prove only that properly blended fine and coarse fibers do not detrimentally affect quality to a significant degree; the findings do not prove that existing blending techniques used in industry today will provide the same degree of homogeneity and product quality. The general consensus that fine and coarse fibers can be blended satisfactorily only within restricted ranges and proportions may be due primarily to the inadequacy of present-day blending systems rather than the incompatibility of fine and coarse fibers in a mixture of cotton fibers. The yearly cotton crop will always consist of significant percentages of fine and of coarse cotton, so if the textile industry wishes to utilize advantageously such cotton qualities and realize cost and economic advantages it should consider seriously improving existing blending operations to include perhaps even pre-blending techniques as suggested recently [6].

Acknowledgment

The authors wish to express their appreciation to the following members of the Southern Utilization Research and Development Division: H. W. Little, Statistician, for guidance in designing the experiment and for statistically analyzing the data; R. T. O'Connor and I. W. Lohmann for analyzing the spectral reflectance data; and others too numerous to name who processed the yarns and fabrics, performed the fiber, yarn, and fabric tests, and made the necessary calculations. Acknowledgment is also made for the cooperation of B. A. Brice and A. M. Smith, Eastern Utilization and Development Division, USDA, in providing spectral reflectance curves. For commercially finishing the fabrics, the authors are especially indebted to J. M. Cheatham, President, and G. E. Fogle, Jr., Lowell Bleachery South, Griffin, Georgia. For the commercial acceptability evaluations, considered to be the most important contribution from the standpoint of practical interpretation of results, the authors gratefully acknowledge the following: W. L. Clement, Jr., Dan River Mills; J. S. Murdock, Pepperell Manufacturing Company; C. M. Cone, Cone Mills Corporation; J. C. Ridenhour, Cannon Mills Company; J. Mitchell, Avondale Mills; and W. R. Bell, Association of Cotton Textile Merchants, who was instrumental in arranging the evaluations.

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Lightfastness and Surface Activity of Dyes: The Effect of Alkylation and of Sulfonation

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Abstract

The systematic changes in lightfastness produced by alteration of surface activity in dyes are described.

Several series of dyes of the sulfonated anthraquinone, sulfonated and unsulfonated azo, azomethin, and *mero*cyanine classes have been irradiated in transparent films and their fading rates and characteristic fading (CF) curves determined.

A marked increase in surface activity of an ionic dye tends to *decrease* lightfastness in normal substrates. A smaller increase in surface-activity, e.g., by introduction of a short alkyl chain, usually *increases* lightfastness. The orientation and number of sulfonate groups affects lightfastness. A more even distribution of such groups or increase in their number in the dye molecule improves the fastness; this rule appears to apply to most acid wool dyes. The effect of normal aggregation of the dyes in the substrate upon their lightfastness is apparently in most cases sufficient to mask differences in their chemical reactivity. The lower the solubility of a dye in a film before setting, the higher is its lightfastness; the higher the solubility, the lower the lightfastness. When dyes are entirely molecularly dispersed, e.g., those in a homologous *mero*cyanine series used here, in collodion, even quite marked changes in length of an attached alkyl chain have almost no effect on fastness.

Introduction

Surface-active dyes, having molecules substituted with long paraffinic chains, are of technical importance in wool dyeing [4] and in color photography [9]. The substituents reduce the diffusion rates of the dyes, thus improving their washfastness on wool and their resistance to migration from one emulsion layer to another in color photographic films. Weak surface activity is also exhibited by planar dye molecules which are sulfonated at only one end or along one side, the remainder of the molecule thus consisting mainly of a large hydrophobic group [5]. Changes in surface activity of dye molecules, caused by either changes in the nature of attached alkyl chains, or changes in the positions of sulfonate groups or the presence of surface-active agents, may be expected to affect lightfastness, because the physical state of the dyes in the substrate will be disturbed [2, 12].

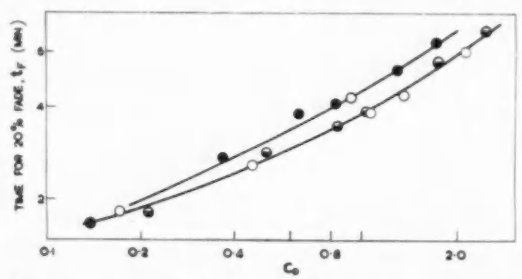


Fig. 1. Characteristic fading (CF) curves for homologous *mero*cyanine dyes (series I) in collodion film. Open circles: C_2 substituent, half-black circles: n-C_7 substituent, black circles: n-C_{16} substituent, C_0 = initial optical density of film.

Very little information has thus far been published upon this aspect of light fading, except brief reports of some of the present work [13, 14], a short statement that in a homologous series of acid dyes lightfastness was found to fall progressively with increasing length of the paraffin chain substituent (C_8–C_{18}) [15], and a report of the effect on lightfastness of changes in sulfonate group orientation in benzeneazonaphthalene dyes [3]. This report indicated that α-naphthol dyes have the highest fastness when the sulfonate group is in position 4, 5, or 6 and the low-

est when it is in position 2 or 8; β-naphthol dyes have lowest fastness when sulfonated at positions 3, 7, or 8. Without more details, however, it is difficult to relate these results to any chemical or physical properties of the dyes.

The application of cationic surface-active agents to direct-dyed cellulosic fibers is a long-established process. These agents affect the surface activity of dyes [5], and in practice they usually reduce lightfastness ([2] and Table I in [12]).

The present work is a study of some of the effects which these various means of altering the surface activity of dyes have upon lightfastness.

The series of dyes is given in Table I.

The results are summarized in Figures 1 through 9 and Tables II through IV.

Discussion

The lightfastness of a dyed material can best be examined by studying two factors: the nature of the fading rate and the change of fastness with change in dye concentration. Both methods can give information about the physical state of the dye, and both have been used in this work.

Fading Rate [1]

The rate of fading of dye in molecularly dispersed form decreases exponentially with time (first-order fade), but the rate of fading of highly aggregated dye remains constant with time (zero-order fade).

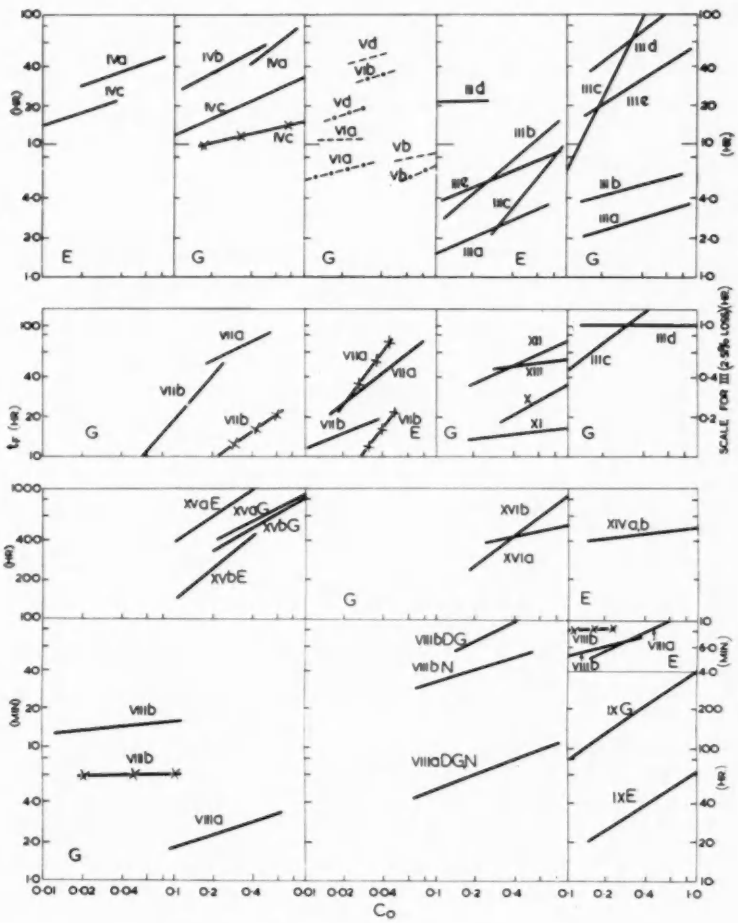
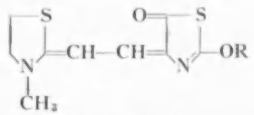


Fig. 2. CF curves for azo and anthraquinone dyes in various films. Films: E = ethylmethylcellulose; D = dyed gelatin; G = cast gelatin; N = dyed nylon. xx: CTAB added; –·–·–: low-power m.v. lamp. ----: xenon lamp. All other tests made with 400 w.m.v. lamp; t_F values are for 10% loss of dye, except where shown. All experimental points are omitted, for clarity.

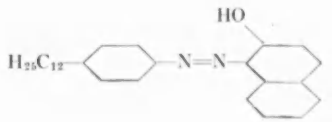
TABLE I. Dyes Used

(X–XIII are color formers from which color-developed dyes were made.)

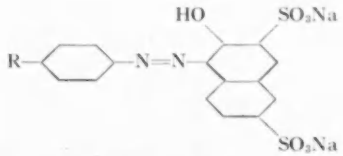


I

a, R = —C_2H_5; b, R = —$CH(CH_3)_2$; c, R = *n*—C_4H_9; d, R = *n*—C_5H_{11}; e, R = —$CH_2C(CH_3)_3$; f, R = *n*—C_6H_{13}; g, R = *n*—C_7H_{15}; h, R = *n*—C_8H_{17}; i, R = *n*—$C_{10}H_{21}$; j, R = *n*—$C_{12}H_{25}$; k, R = *n*—$C_{14}H_{24}$; l, R = *n*—$C_{16}H_{33}$; m, R = —$(CH_2)_2Ph$.

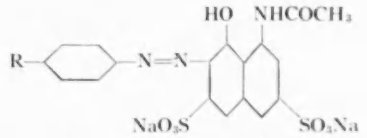


II



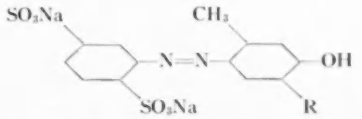
III

a, R = —H; b, R = —CH_3; c, R = *n*—C_4H_9; d, R = *n*—$C_{12}H_{25}$; e, R = *n*—$C_{16}H_{33}$.



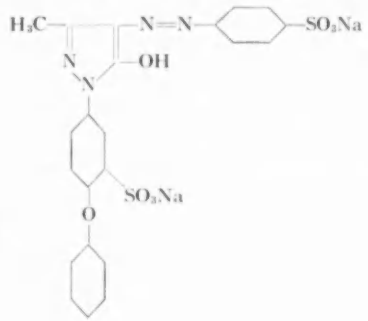
IV

a, R = —H; b, R = *n*—C_4H_9; c, R = *n*—$C_{12}H_{25}$.



V

a, R = —H; b, R = —CH_3; c, R = —$CH(CH_3)_2$; d, R = —$C(CH_3)_3$.



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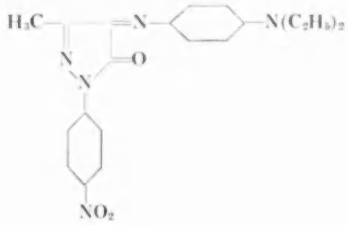
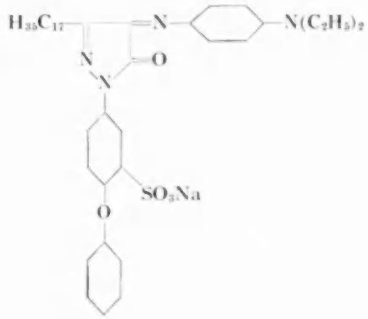


X



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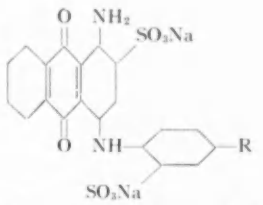
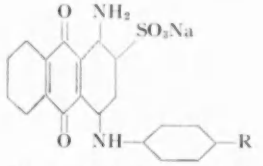


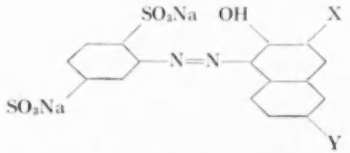
XV

a, R = —CH_3; b, R = *n*—$C_{12}H_{25}$.



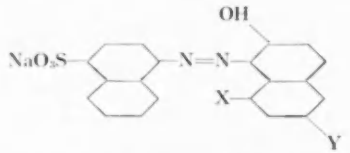
XVI

a, R = —H; b, R = *n*—C_4H_9.



XVII

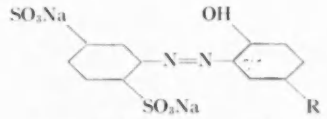
a, X = —H; Y = —SO_3Na; b, X = —SO_3Na, Y = SO_3Na.



XVIII

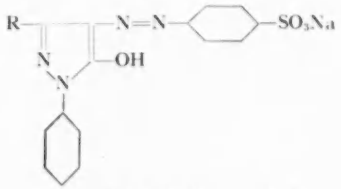
a, X = —H, Y = —H; b, X = —SO_3Na, Y = —SO_3Na.

TABLE I Continued



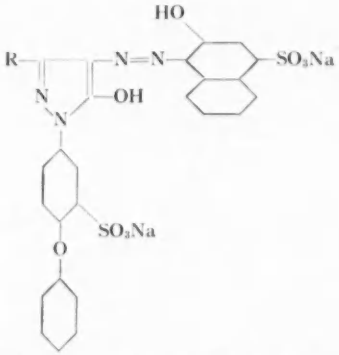
VI

a, R = —CH_3; b, R = —$C(CH_3)_3$; c, R = —$C(CH_3)_2CH_2C(CH_3)_3$



VII

a, R = —CH_3; b, R = *n*—$C_{17}H_{35}$.



VIII

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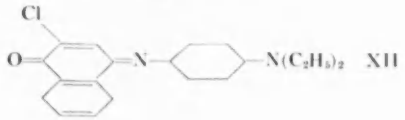

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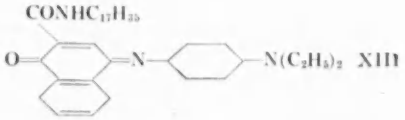

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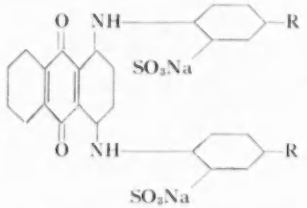
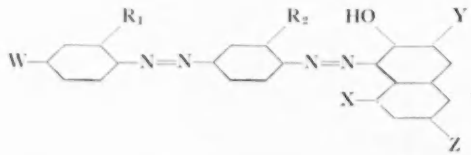


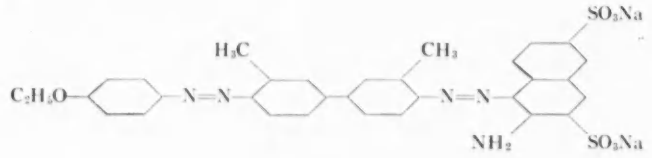
XIV

a, R = —CH_3; b, R = *n*—C_4H_9.

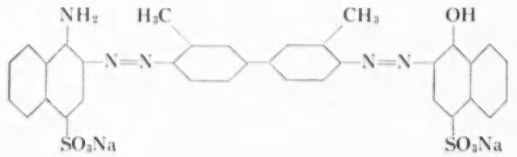


XIX

a, W = —SO_3Na, X = —SO_3Na, Y = —H, Z = —H, R_1 = —CH_3, R_2 = —CH_3; b, W = —H, X = —H, Y = —SO_3Na, Z = —SO_3Na, R_1 = —CH_3, R_2 = —CH_3; c, W = —H, X = —H, Y = —SO_3Na, Z = —SO_3Na, R_1 = —H, R_2 = —H.



XX



XXI

TABLE II. Comparative Fading Times in Mercury Vapor and Xenon Lamps

Dye	Substrate	Fading times, percent loss of dye, and lamp		
		Hg	Xe	
		10%	5%	10%
IIIa	Gelatin	1.8	*ca.* 9	
IIIb		4.0	23	
IIIc		1.3	2.5	
IIId		20	46	
IIIe		4.0	27	
VIIIa	Gelatin	2.6(min.)	25(min.)	50(min.)
VIIIb		15 (min.)	180(min.)	
VIIIb (+ CTAB)		6 (min.)	*ca.* 30(min.)	

Gelatin films: cast, for Hg lamp; hardened and dyed for Xe lamp (except VIIIa, b). The times in Hg lamp are approximate, estimated by interpolation for films of the same shade depths as used in Xe lamp. Fading times in hr., except for VIIIa, b.

TABLE III. Monolayer-Forming Data for Sulfonated Dyes [5]

Dye	Molecular cross-sectional area (A*)		
		Found, on:	
	Calc. from model	Water alone	4 *M* NaCl solution
IVa	65	n.f.	n.f.
IVb	65	n.f.	n.f.
IVc	65	17	53
XIXa	120	n.f.	42
XIXc	65	n.f.	61

* The nearer the measured value is to the calculated, the more stable is the monolayer; low measured values represent partial solution of the film molecules.
n.f. = no film formed.

Fastness–Concentration Relation [2, 12]

When the logarithm of the time (t_F) required for a given percentage loss of dye by fading (or the fastness grade number, which has been shown to be equivalent to log t_F [12]), is plotted against log dye concentration, in a range of concentrations, a straight line is usually obtained.

This type of curve is termed a characteristic fading[1] (CF) curve if log t_F values are used (*cf.* Figures (1–3, 7) and a characteristic fastness grade (CFG) curve if fastness grades are used (*cf.* Figure 6).

It can be shown in theory and demonstrated by experiment [2, 12] that the slope of such a curve depends upon the change in size distribution of dye particles with concentration. When there is no change in size distribution (for example, in the case of true molecular dispersions), or uniformly mixed and sampled pigment dispersions, the curve is horizontal.

Fading probably occurs mainly at the air-exposed surface of dye particles, so that the ratio of surface to weight of dye determines the fading rate. If the particle size distribution is constant over a range of dye concentrations, the surface–weight ratio, hence the fading rate, is constant also. This explains the horizontal curve. Usually, however, the curves have positive slope (i.e., fastness improves with rise in concentration, as is well known), and this is believed to be the result of an increase in the proportion of large particles with dye concentration. This increase *reduces* the surface–weight ratio and thus reduces the fading rate also. Large particles fade more slowly than small ones.

A fuller explanation of these effects is given in earlier papers from this laboratory [2, 12, 14].

Effect of Increase in Length of Attached Paraffin Chains

General Results

Nonionic dyes. Evidence has been given [1, 2] that the *mero*cyanine dyes, series I, are apparently in molecular dispersion when cast in collodion films. Fading is very rapid, and the rate is almost independent of the chain length of the alkyl substituent

[1] This term is now preferred to the earlier term "characteristic fading order."

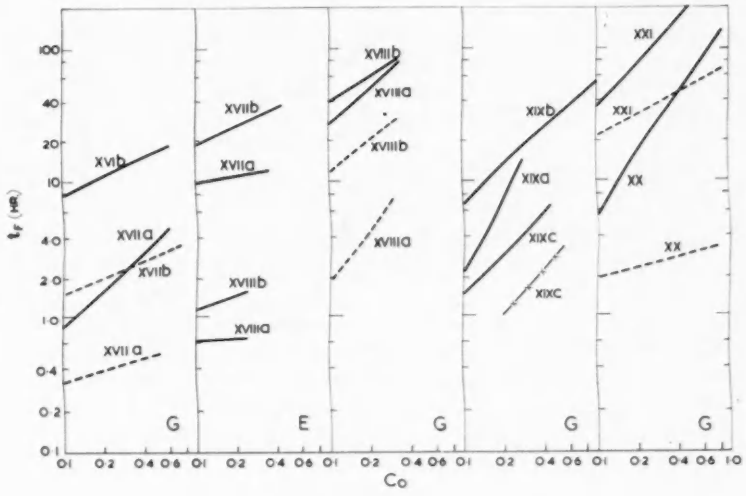


Fig. 3. CF curves for azo dyes in ethylmethylcellulose and gelatin. Films: EMC = ethylmethylcellulose; G = gelatin (cast), ---: Curves for 5% loss of dye, ——: Curves for 10% loss of dye, xx: CTAB added. For XVIb, read XVIIb; vertical scale $\times 10^{-1}$ for XVIIa, bE.

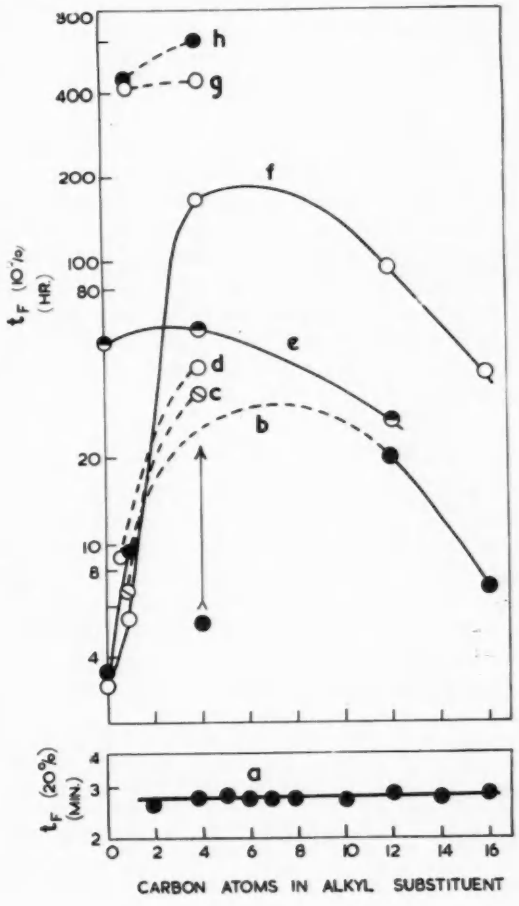


Fig. 4. Relation between length of paraffin chain substituent in dyes and time (t_f) for percentage fade shown; a, nonionic dyes; b–h, sulfonated dyes. Dyes and films. (E = ethylmethylcellulose; G = gelatin). a = I (collodion); b = IIIE; c = VG; d = VIG; e = IVG; f = IIIG; g = XIVE, h = XVIG. t_F values in each series measured at constant C_0 values; the shape of these curves will of course vary a little with the particular value of C_0 chosen.

(Figures 1 [2] and 4); thus apparently the substituent does not influence the physical state of the dye. This belief is supported also by a study of the visible light absorption curves of the dyes in the films. They each have a single rather broad symmetrical peak about 4550 Å, which we identify with the monomeric dye (the x-band [16]).

Ionic dyes. As already stated, the physical state in the substrate, and therefore the fading rate, of a sulfonated dye applied from water is expected to vary with the surface activity of the dye. In fact, there appears to be a general tendency for fastness to increase with chain length from C_0 up to about C_4, and then to fall (Figures 2, 3, and 4). In some cases the high surface activity conferred by a very long chain markedly reduces fastness.

These effects are probably caused by changes in the ratio of molecularly dispersed and aggregated

[2] The increasing slope of these curves with increase in concentration is believed to be the result of the slowness of penetration of moisture into this hydrophobic substrate. Fading is very rapid, and with increase in dye concentration it is increasingly difficult for moisture to penetrate rapidly enough to maintain the fading reaction (*cf.* [1], p. 388, footnote).

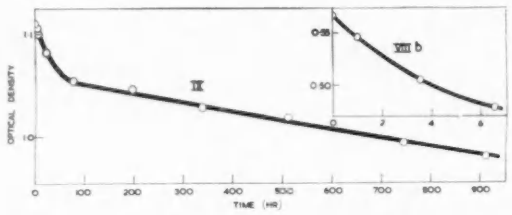


Fig. 5. Fading rate curves for azopyrazolone dyes in gelatin under filtered m.v. illumination (4358 Å).

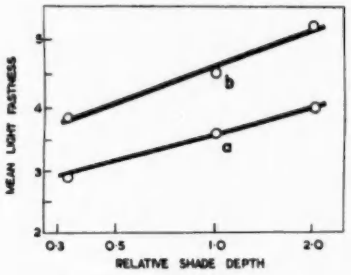


Fig. 6. CFG (characteristic fastness grade [12]) curves for (a) "unsymmetrically" and (b) "symmetrically' sulfonated acid dyes on wool. C.I. data: mean values from Table IV. Note: in the *Colour Index* the weakest depths are given as "$\frac{1}{8}$–$\frac{1}{2}$" of the standard. Here they are assumed to be $\frac{1}{4}$ of standard depth.

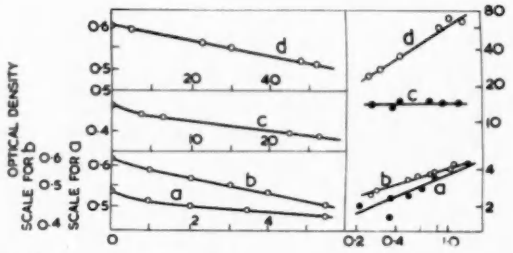


Fig. 7. Effect on lightfastness of compatibility (in liquid state, before setting; fasting tests made on dried films) of dye and substrate. a: IIId (sulfonated dye, $C_{12}H_{25}$ chain) in collodion, b: II (unsulfonated dye, $C_{12}H_{25}$ chain) in collodion, c: IIIc (sulfonated dye, C_4H_9 chain) in collodion, d: II in ethylmethylcellulose. Left: fading rate curves. Right: CF curves.

dye. Dye molecules with short chains may be present mainly as aggregated particles or micelles, which increase in size, and therefore in lightfastness, with increase in chain length. When the chain is lengthened beyond about C_{12} it can form not only micelles but also a condensed unimolecular film, which becomes more stable and more uniformly spread in the substrate as the chain length increases [5]. The dye in this unimolecular film fades more rapidly than in the micelles. Hence the fastness tends to be low with the long-chain dyes.[3]

Even a pair of methyl groups can significantly affect fastness. Thus it was found (results not shown here) that XIXb fades more rapidly than XIXc on cellulose film and more slowly than XIXc on gelatin (in accordance with the reversal rule previously described [10]), but only if phenol is present as a disaggregating agent. In its absence XIXb faded the more slowly on both substrates. Here aggregation is masking the effect of the difference in nature of fading on cellulose (oxidation) and gelatin (reduction).[4]

Effects in the Azopyrazolone Series

These dyes show remarkable differences in fastness; e.g. VIIIa and b fade about 800–1000 times more rapidly than IX (Figure 2). The reduction rates in water differ very little; indeed, VIIIa reduces rather more *slowly* than IX (see "Materials and Methods" below) so that the fading rate differences in gelatin, in which the dyes are probably faded by reduction [10], are unlikely to be due to differences in reactivity and appear to be due to differences in physical state. There is a difference in absorption spectrum between VIIIb and IX, but when films of these dyes are faded by the 438 Å mercury vapor line, which is close to the point of intersection of the absorption curves of the two particular depths of dyed film used here, the relative fading rates are not much altered (Figure 5). VIIIb still fades more rapidly, even though it is absorbing less radiation. VIIIa and b have first-order fading rates (Figure 3 in [1]) and CF curves of low slope. IX fades with less than first-order rate (Figure 9 in [1]) and has the steeper CF curves. All these facts suggest that IX is highly aggregated in the films, but films of VIIIa and b contain much monodisperse dye.

Azomethin Dyes

In these color-coupled dyes there is a marked tendency for alkylation to reduce lightfastness at

[3] Though the dye in micellar form would fade slowly, its presence would not, when unimolecular material is also present in large proportion, increase the fastness as normally measured. The reason is that fading rates are measured, both here and in technical practice, in the early stages, when the smaller dye particles are decomposing.

[4] As stated in a later erratum note, the names of these two dyes in [10], Table II, should be reversed.

higher shade depths (Figure 2). In these cases there are small differences within the dye pairs in structure and in position of absorption peaks (X, 5250 Å; XI, 5400 Å; XII, 6500 Å; XIII, 6700 Å).

Effect of Position and Number of Sulfonate Groups

If a planar dye molecule has a sulfonate group or groups at only one end, or along one edge, it can exhibit weak surface-active properties, even if no alkyl chains are present [5]. Its degree of surface activity, i.e., the stability of the monolayer films it forms on water, also appears to increase with the height of the hydrophobic part of the molecule in the layer (Table III, *cf.* [5]). With this principle as a guide, examination of the present results (Figure 3; *cf.* dyes XIXc and a, XX and XXI, the second of each pair being the less surface active) and of all

TABLE IV. Relation between Sulfonation Pattern and Lightfastness* on Wool (Data from Color Index)

C.I. Number		Sulfonation pattern*		Lightfastness and relative depth†			
		Orientation	Symm. or unsymm.	½ to ½	1	2	
Benzeneazobenzene and Benceneazodiphenylamine dyes							
Acid Yellow 36	13065	3′	Unsymm.	2	3	4	(C)
Acid Orange 5	13080	4′	Unsymm.	2	3	3–4	(C)
Acid Yellow 9	13015‡	4′, 3	Symm.	4	4–5	5	(C)
Benzeneazo-2-naphthol dyes							
Acid Orange 12	15970	6	Unsymm.	3	4	5	(C)
Acid Orange 7	15510	4′	Unsymm.	3	4	4	(C)
Acid Orange 14	16100	3, 6	Unsymm.	2	3	3–4	(C)
Acid Orange 10	16230	6, 8	Symm.	4	4–5	5–6	(C)
1-Naphthylamine-1-naphthol dyes							
Acid Red 20	14830	5	Unsymm.	2–3	3	3–4	(C)
Acid Red 3	14910	3, 6	Unsymm.	2	3	3	(C)
Acid Red 14	14720	4′, 4	Symm.	3	3	4	(C)
Acid Red 12	14835	4′, 5	Symm.	3	4	4–5	(C)
1-Naphthylamine-2-naphthol dyes							
Acid Red 14	15625	5′	Unsymm.	1–2	2	2–3	(C)
Acid Red 17	16180	3, 6	Unsymm.	2	3	3	(C)
Acid Red 25	16050	4′, 8	Symm.	2	3–4	4	(C)
Acid Red 44	16250	6, 8	Symm. (?)	2	3	4	(C)
Acid Red 88	15620	4′	Unsymm.	2	2–3	3	(C)
Acid Red 13	16045	4′, 6	Symm.	2–3	3	3–4	(C)
Acid Red 18	16255	4′, 6, 8	Symm.	3	4	4–5	(C)
Acid Red 41	16290	4′, 3, 6, 8	Symm.	3–4	4–5	5	(C)
Anthraquinone dyes							
Acid Blue 43	63000	2	Unsymm.	4–5	5	5–6	(B)
Acid Blue 45	63010	2, 6	Symm.	5	5–6	6	(B)
4-Tolylaminoanthraquinone dyes							
Acid Violet 43	60730	4(2′)	Unsymm.	5	5	5–6	(C)
Acid Blue 27	61530	4(2′)	Unsymm.	4	4–5	5	(C)
Acid Blue 47	62085	4(2′)	Unsymm.	5	5	5–6	(C)
1:4-Ditolylaminoanthraquinone dyes							
Acid Green 25	61570	1(2′), 4(2′)	Symm.	6	6	6–7	(C)
Acid Green 38	62550	1(2′), 4(2′)	Symm.	6	6	6–7	(C)

* Unsymm. (unsymmetrical) and Symm. (symmetrical) refer respectively to constitutions favoring orientation of the molecule perpendicular to the surface or flat to obtain closest sulfonate group-surface contact (judged by models); see text.

† (B), (C), = British and Continental testing methods, respectively.

‡ With this exception, all the dyes in each group have identical numbers and arrangement of aromatic nuclei.

relevant data for acid dyes on wool in the Colour Index (Table IV, Figure 6), shows that lightfastness is usually improved by altering the orientation of sulfonate groups so as to reduce surface activity of the dye. Presumably such alteration reduces the amount of molecularly dispersed dye and increases the amount aggregated in the substrate.

It also appears that an increase in number of sulfonate groups can improve lightfastness. In some cases this increase can reduce surface activity (*cf.* XVIa→XVa; XVIIIa→b), but in other cases the increase cannot reduce surface activity (e.g., XVIIa→b), because neither dye in the pair can be surface active.

These effects of altering the position of sulfonate groups cannot be due only to variations in susceptibility of the dye molecule to photochemical degradation. If they were, the ranking of the dyes in each pair would be reversed as between the two substrates (ethyl methyl cellulose and gelatin) [10], but it is not. It must be assumed that increased sulfonation improves the stability or the size of the dye micelles in the substrate. Without new information on the nature of the dye micelles it is difficult to visualize how this can occur. Possibly the micelles have water associated with the ionic groups, as in the "J-aggregates" or giant molecules of photographic sensitizing dyes [7, 11], but do not have the chain-like structure of the J-aggregates. A relevant fact in this case is that layers of basic dyes deposited by sublimation *in vacuo* are usually amorphous, but they appear to take up a more ordered arrangement in presence of water vapor [17].

Effect of Cationic Agent (Cetyltrimethylammonium Bromide, "CTAB")

Highly surface-active ionized substances in water form both ionic micelles in the bulk solution and a unimolecular film at the surface. It is well known that cationic agents can form mixed micelles with anionic dyes in solution, and they can also promote formation of unimolecular films of surface-active dyes [5]. Both effects probably contribute to the action of CTAB on lightfastness. Usually it reduces fastness; the increase in molecular dispersion probably in these cases promotes a more rapid fade. When, however, the dye is already largely monodisperse and thus has low fastness (VIIIb on EMC), fastness is increased by addition of CTAB. This result could be attributed to the slower fading of the micelles thus formed.

Other photochemical effects may occur in such systems; e.g., enhanced rate of free radical formation by the dye–agent complex, but no evidence of such effects can be obtained with the present tests.

Effect of Compatibility of Dye and Substrate

Tests with azo dyes (II, IIIc and d) in two films (Figure 7) show that when dye and substrate are similar in type, i.e., both hydrophobic (unsulfonated, or long alkyl chain dye, in collodion) or hydrophilic (short-chain sulfonated dye in EMC), there is a high proportion of molecularly dispersed dye, and fading is rapid. Opposite conditions, i.e., hydrophobic dye in hydrophilic film, increase the proportion of aggregated dye and improve fastness.

Materials and Methods

Dyes

Purified samples were used. The compounds (X, XI, XII, XIII) were supplied by Ilford Ltd. in the form of dyed gelatin.

Films

The preparation of collodion, ethylmethylcellulose (EMC), and gelatin films has been described [1, 2, 8]. Most of the films were prepared by casting from a colored dope. For comparison, a few were prepared by dyeing precast material. The two methods gave similar fading results, in that relative differences among dyes were much the same, but the dyes in the cast films usually faded more slowly than these in the dyed ones.

Pure cetyltrimethylammonium bromide (CTAB) was added in quantities equimolar with the dye; larger amounts caused film splitting and peeling.

Relative concentration (C_o) values for collodion films (series I) and films of dyes V and VI are given in terms of the actual optical densities of the unexposed colored films; for other films, they are given as the optical densities of extracts of unexposed films in 50% (vol./vol.) aqueous pyridine. Portions of film of the same size as those used for exposure were cut, dissolved in 10 cc. of solvent, and measured in a 1-cm. optical cell. It is assumed that change in the length of a paraffin chain substituent does not have a significant effect on the molar extinction coefficient of a dye and that in collodion and in pyridine the dyes are disaggregated; therefore equimolar amounts

of all dyes in a given series should give identical C_0 values.

Absorption spectra and fading rates were measured on a Unicam SP500 spectrophotometer.

Irradiation Procedure

Illumination was by 400-watt mercury vapor lamp [8] (250-watt, with series resistance, for V and VI). A few tests were made with a xenon lamp (*cf.* [6]), which was obtained after the main investigation had been completed. This lamp gives a continuous spectrum resembling skylight. Three sets of dyes were exposed with this lamp. In each set the absorption bands differ a little from dye to dye, but they cover the principal mercury vapor emission lines. No significant difference is in fact found (Table II, Figure 2) in the ranking order as between the two lamps. Slight changes in light absorption due to aggregation are therefore unlikely to influence any of the later results.

Oxidation and Reduction Rates

Fading appears usually to occur by oxidation on non-protein substrates and by reduction on proteins [10]. In the present investigation several comparisons were made of rates of oxidation or reduction of the dyes in solution and their fading rates on the two types of substrate. The results appear to show, as expected, that there is not necessarily any simple relation between the stability of a dye in solution and its lightfastness. This can in fact be seen from the fading results alone. Thus, if the fastness differences in any given series of dyes were due only to differences in chemical reactivity, the ranking should always be in the reverse order on gelatin, compared with ethylmethylcellulose; yet in nearly all cases this is not so, and the dyes in most series rank in the same order on both substrates.

Acknowledgments

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Manuscript received April 19, 1960.

Note

Since the present work was completed, Weissbein and Coven [TEXTILE RESEARCH JOURNAL **30**, 58, 62 (1960)] have demonstrated, by electron micrography, that among certain direct cotton dyes in cellulose, those with the highest lightfastness are the most highly aggregated.

Some Studies on the Cross-Linking of Cotton Cellulose[1]

Part I: Chemical and Physical Aspects

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Abstract

The currently-used types of cross-linking agents and some of their effects on cotton are discussed. The primary weaknesses or shortcomings of the finishes achieved with these agents are pointed out. It can be concluded either that the ideal cross-linking agent for cotton has not been found or that the best technique of application has not yet been discovered. However, considerable success is being had in producing minimum-care fabrics by the use of many cross-linking agents, especially the N-methylol type.

Although cross links through primary covalent bonds are largely responsible for the observed physical changes in cross-linked cotton fiber, secondary valence cross links also may produce significant changes, some of which appear to be rather durable. Evidence is presented which indicates that polymer formation produced concurrently with cross-linking improves the over-all minimum-care properties of cotton fabric, although polymer formation alone does not improve the wrinkle recovery. Cross-linking agents which are capable of forming thermosetting resins generally are required in somewhat larger add-ons to produce wrinkle recovery angles in the practical range than are those agents that do not form thermosetting resins. The extent of permanent set is related to the extent of cross-linking. Moisture regain and density of the cross-linked cottons are more dependent upon the state of fiber swelling at the time of cross-linking than upon the extent of cross-linking.

COTTON has remarkable mechanical properties. These properties arise from the great length : width ratio of its component cellulose molecules, the highly oriented disposition of these molecules within the fiber, and the molecular rigidity resulting from the multi-ring structure of the cellulose molecules. A consideration of the length of an average cellulose molecule in cotton, e.g., 2–3 μ, and that of a fiber, 25,000 μ, indicates that the high tenacity shown by a cotton fiber must arise from lateral bonding between molecules. Except for accidental physical entanglement of molecular aggregates of the cellulose, the lateral binding of the molecules is ordinarily limited to hydrogen bonding and to van der Waals forces. The phenomena of stress relaxation, creep, delayed recovery, and permanent set attest to the occurrence of molecular flow in stressed cellulosic fibers. The most effective method of decreasing the extent of molecular flow, thus improving the elastic recovery and dimensional stability of cellulose fibers, appears to be through the introduction of primary covalent bonds between molecules. Rearranging the hydrogen bonds between cellulose chains to more favorable positions likewise stabilizes the spatial relationship of the molecules thus affected.

Because of the importance of the properties conferred by such chemical modifications, an ever-increasing amount of thought and effort has been devoted to the study of cross-linking of cellulose during the past three decades or more. Success was first met in the finishing of viscose rayon; later, spectacular results were obtained with cotton. This work has led to a large number of excellent and valuable finishes which give dimensional stability, reduced maintenance, quick drying, and many other

[1] Presented in part at the Gordon Research Conference on Textiles, New London, N. H., July 13–17, 1959 and at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 13–18, 1959.

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valuable properties. However, the various modifications also produce certain undesirable effects, such as reduced tear strength, breaking strength, and abrasion resistance. It is literally true that cross-linking agents modify almost every property of cotton fiber and fabric. In spite of the remarkable progress which has been made, it is clear that the ideal resins or cross-linking chemicals are not yet available, nor have the application techniques been perfected. A better knowledge of what happens in the fiber and fabric in the cross-linking process is badly needed.

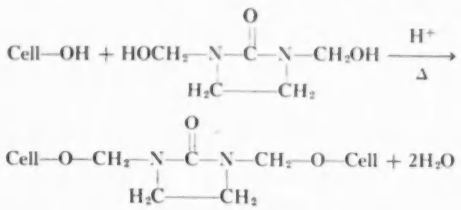
This paper considers certain broad aspects of cross-linked cotton cellulose. Part I includes discussions of the types of cross-linking reagents of practical and theoretical interest; the nature, type, and extent of the cross-links introduced; and the resultant variation in properties of the reaction product. In Part II, the results of a series of microscopical observations on cross-linked cotton fibers and related materials are presented. It is believed that such studies are an important step in the process of developing minimum-care cotton textile materials possessing properties approaching the ideal for the end-use desired.

Types of Cross-Linking Agents

N-Methylol Compounds.

Most of the textile chemicals used today to cross link cotton cellulose are the N-methylol type compounds. The nature of these compounds has been changed only slightly since their introduction. The following compounds illustrate the type of structural changes made: dimethylolurea, trimethylolmelamine, dimethylolethyleneurea, dimethyl ethyl triazone [1,3-bis(hydroxymethyl)-4,4,6,6-tetrahydro-5-ethyl-s-triazin-2-(H)-one], and 4,5-dihydroxy-1,3-bis(hydroxymethyl)-2-imidazolidinone.

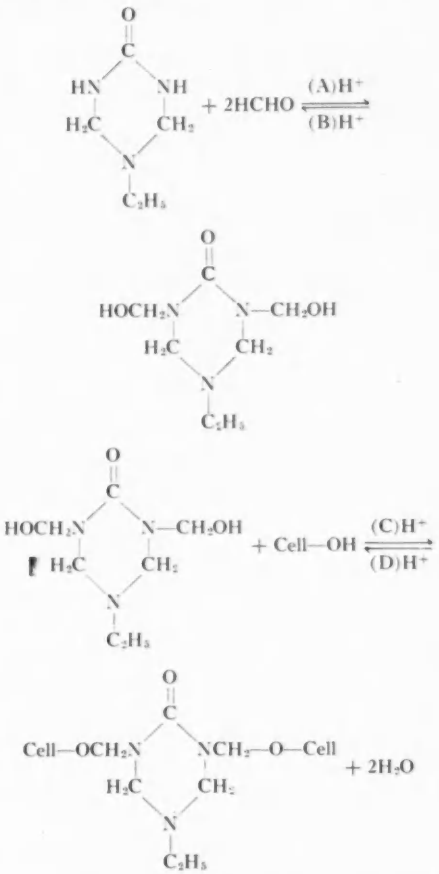
The reaction of these compounds with cellulose can be represented with dimethylolethyleneurea.



Although all of the N-methylol type compounds react with cotton under acid-catalyzed conditions, the properties of modified fabric differ quite significantly. Some of these differences will be discussed.

General Limitations of N-Methylol Compounds

N-methylol type compounds have a serious weakness—lack of durability—that has gone almost without attention. It should be remembered that the formation of the methylol compounds and the reaction of these compounds with cellulose are both reversible reactions. These reactions are represented with ethyl triazone.

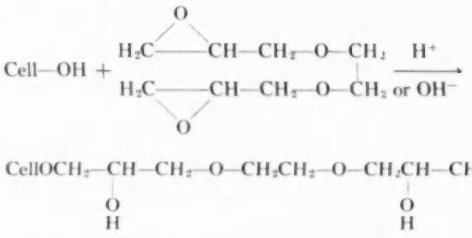


The reversibility of the first reaction is well known. It can be demonstrated easily by merely heating an aqueous solution of the dimethylol compound (even without catalyst) and detecting the formaldehyde that is released. Reaction of the methylol compounds with cellulose during cure at elevated temperatures is driven to completion by loss of water. The net

reaction rate approaches zero on cooling and removal of catalyst; however, the reaction rates are still high enough to produce certain effects during storage and use of the fabric. After the fabric is processed, it picks up moisture, and the presence of this water not only shifts the equilibrium in the direction of fewer cross links but also liberates methylol groups, which allows formation of new cross links. Evidence that all four of the reactions take place after the fabric is finished can be given by the following. Treated fabric stored in bolt form takes on a "set" corresponding to the curves in the bolt. This is the result of broken cross links by the reversible Reaction D and the re-establishment of new ones through Reaction C. This process is accelerated by the presence of acid catalysts. Stored fabrics release formaldehyde. This is a result of the reverse Reactions D and B. These same two reactions are indicated by a decrease in nitrogen content upon laundering. Increased chlorine retention on repeated launderings is probably due to the primary and secondary amido groups formed as a result of the reversible reactions. These amido groups, especially the primary, are capable of forming a chloramide. These shortcomings or limitations of N-methylol type finishing agents can be minimized by a thorough wash after curing to remove catalyst and by storage in a cool dry atmosphere. A thorough cure to drive the reaction to completion will reduce the initial chlorine retention.

Compounds Containing Epoxy Groups

This class of compounds is currently receiving attention in both research and commercial application [7, 18]. These compounds have two especially attractive features—durability and no chlorine retention (at least for those that do not contain chlorine-retaining groups within the molecule). Many epoxy compounds react with cotton through acidic and basic [10] catalysis. The acid-catalyzed ones often lead to excessive degradation of fabric strength. These are generally applied by the pad, dry, and cure process. Base-catalyzed compounds can be reacted by this same process or they may be reacted by omitting the drying and curing operation. It is highly probable that for equivalent degrees of cross-linking the losses in fabric strength will be comparable. It appears that one limiting factor in the use of epoxy compounds is that the epoxy group or groups must be at terminal positions where basic catalysis is used. The reaction of a diepoxy compound with cellulose is illustrated in the following equation:



Vicinal halohydrins are capable of forming epoxy compounds *in situ* in the presence of strong bases and therefore may be used in place of epoxy compounds when the reaction is to be carried out under basic conditions. Epoxy compounds can cross link and fix cotton fibers in essentially a collapsed condition by the dry and cure process or in a swollen state when the dry and cure operations are omitted.

Several halohydrins and epoxy compounds are being investigated. They include tris(epoxypropyl)amine, *N,N,N*-tris(3-chloro-2-hydroxypropyl)-amine, butadiene dioxide, the dichloropropanols, and epichlorohydrin.

In general, these reagents when reacted with cotton in strong alkali solutions at room temperatures produced good wet but decreased dry wrinkle recovery and increased moisture regain. Wrinkle recovery angles were measured on some of these fabrics in the dry state, in the water-swollen state, and in the alkali-swollen state (20–25% aqueous sodium hydroxide). In each case the best wrinkle recovery was obtained in the water-swollen samples. The general performance trends of such fabrics may be illustrated as in Figure 1 by the wet and dry wrinkle recovery of cotton print cloth cross linked with *N,N,N*-tris(3-chloro-2-hydroxypropyl)amine in the presence of mercerizing-strength caustic [11].

In contrast to the above, the epoxides which can cross link cellulose by the dry and cure process using acid catalysts produce both dry and wet wrinkle recovery. By this method, using $Zn(BF_4)_2$ or $Zn(NO_3)_2$ as catalysts with butadiene dioxide or tris(epoxypropyl)amine, wet and dry wrinkle recovery angles in the range of 280–300° (W + F) have been imparted to print cloth.

Acetals

The modification of cellulosic fibers with formaldehyde has been studied intermittently for over fifty

years [2, 17]. As early as 1929 it was suggested that cellulose may be cross-linked with formaldehyde [12]. Apparently the developments with formaldehyde have not been practiced commercially to any great extent. Several organizations are currently seeking to develop suitable methods for large-scale application, and it appears imminent that finishing cotton with formaldehyde will at last be feasible. Formaldehyde is an attractive cross-linking agent from a number of points of view. It is non-chlorine-retentive, very efficient, cheap, and durable to acidic, neutral, and alkaline laundry conditions. Its primary weaknesses are difficulty in duplication of a finish and loss in fabric strength. Current work at this laboratory indicates that loss of excessive strength can be overcome. Formaldehyde cross links cellulose by formation of methylene-ether bridges, an amazingly stable acetal link, and perhaps by some polyoxymethylene bridges.

Polymeric formals have been employed recently to cross link cellulose [8]. Evidently the cross links are formed through transacetalization. The cross links probably consist of methylene bridges produced by formaldehyde regenerated under the acidic conditions and of poly (formal) chains. The reaction of cellulose with poly (oxydiethyleneformal) to produce poly (formal) bridges may be represented by

$$\text{Cell—OH} + \text{HOCH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2)_n\text{OH} \longrightarrow$$
$$\text{Cell—OCH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2)_n\text{O—Cell} + \text{H}_2\text{O}$$

Other acetal-producing reagents have been reacted with cellulose. Glyoxal and α-hydroxyadipaldehyde are offered commercially as shrink-control agents for cotton. The exact type of bridge formed by cross-linking with dialdehydes is not known, but it may be represented by the folowing structure:

$$\text{Cell—OH} + \text{OHC—CHO} \longrightarrow \text{Cell—O—}\underset{\displaystyle \text{C=O}}{\overset{\displaystyle \text{H}}{\underset{|}{\overset{|}{\text{C}}}}}\text{—O—Cell}$$
$$\text{H}$$

The acetals and polymeric formals produce good wet and dry wrinkle resistance. Recovery angles up to 300° (W + F) have been obtained. Dialdehydes, such as glyoxal, usually discolor cotton fabric when applied by the pad, dry, and cure process.

Poly(1-Aziridinyl) Compounds

Tris(1-aziridinyl) phosphine oxide, referred to as APO, has recently been used in making cotton flame resistant [14] and to impart wrinkle resistance [3]. This compound, when used with zinc fluoroborate as the catalyst, produces fabric with excellent wash-and-wear properties. The ether links formed through opening of the aziridine rings make this finish extremely durable to all types of laundering conditions. Actually, there is no known method of removing the finish. Cross-linking of cellulose with APO can be indicated as follows:

$$\text{Cell—OH} + (\text{CH}_2\text{CH}_2\text{N})_3\text{P=O} \longrightarrow$$

$$\text{Cell—O—CH}_2\text{CH}_2\text{N—}\overset{\displaystyle \text{O}}{\underset{|}{\overset{\|}{\text{P}}}}\text{—N—CH}_2\text{CH}_2\text{—O—Cell}$$
$$\text{H} \quad \text{N} \quad \text{H}$$
$$\text{H}_2\text{C}\text{———}\text{CH}_2$$

The remaining ring may also react with cellulose or enter into reactions leading to polymer formation. White fabrics reacted with APO by the current

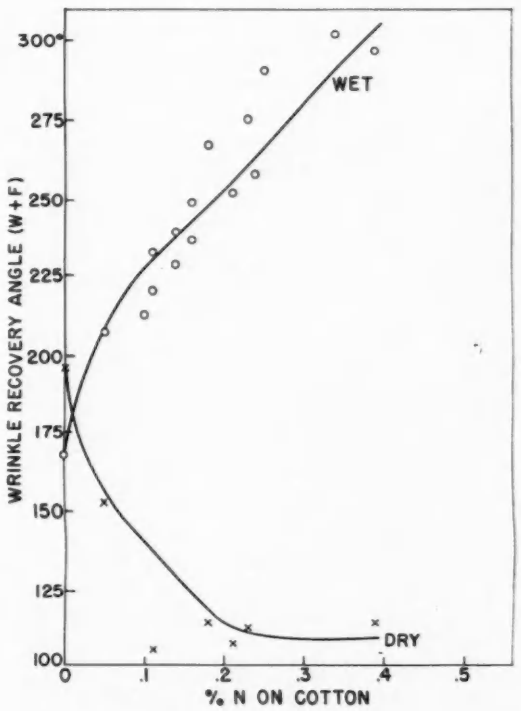
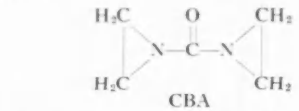


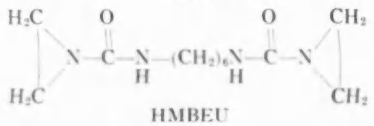
Fig. 1. Wrinkle recovery of print cloth reacted with N,N,N-tris(3-chloro-2-hydroxypropyl)amine in presence of mercerizing strength caustic solution.

technique yellow slightly when bleached with hypochlorite and then ironed. However, the yellowing is not expected to be a deterrent to the use of APO in colored goods. The cost of APO will limit its use until it is made in larger quantities and on a more competitive basis.

Several other 1-aziridinyl compounds are being examined in the laboratory as possible cross-linking agents for cotton. These include carbonyl bisaziridine (CBA) and hexamethylene bisethyleneurea (HMBEU).



CBA

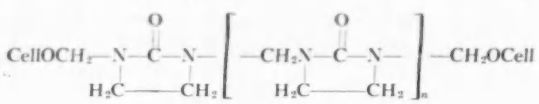


HMBEU

Nature and Type of Cross Links

Polymer Formation Concurrently with Cross Linking

Because of the possibility of polymer formation and side reactions, the precise nature, number, and location of the usual cross links in cotton are not known. Most, if not all, of the cross-linking agents used for finishing today can polymerize under the exact conditions used to cross link the cotton. Of course, the extent of self-polymerization varies tremendously. This has led to discussions on the relative merits of single-unit cross links and polymeric cross links. Cross links formed with formaldehyde have been studied and are thought to consist mainly of methylene bridges [19]. Urea formaldehyde (UF), which can produce thermosetting resins, has been reported to cross link cotton with an average of two urea residues per cross link [20]. More recently, the reaction product of dimethylolethyleneurea (DMEU) and cotton was studied [5] to determine the average length of the cross links. Zinc nitrate, a typical latent acid catalyst, was used in the work. It was concluded that there are 1.5 ethyleneurea residues per cross link. Under the usual reaction conditions, this compound does not form insoluble thermosetting resins. The average cross-linking of cellulose is represented in the following structure, where n is 0.5. The value of n was found to vary

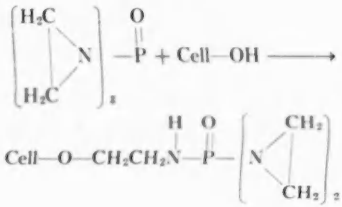


slightly with the amount of material reacted with the cotton . But the main point to note is that the cross link did not uniformly consist of single ethyleneurea residues. Under the usual conditions for reaction, DMEU produces a practical wrinkle recovery angle with slightly lower add-ons than UF. This may be attributed to the more extensive cross-linking by the DMEU.

Polymer formation concurrently with cross-linking is an asset to at least some finishes. When essentially monomeric trimethylolmelamine is applied to cotton print cloth by the conventional process of pad, dry, and cure using a latent acid catalyst, dry wrinkle recovery angles of about 250–280° (W + F) are obtained with about 6–10% add-on of finish. Higher wrinkle recovery angles can be obtained by using a freshly prepared formic acid colloid of the same compound [1]. The colloid finish is obtained by dissolving equal weights of trimethylolmelamine and formic acid in water, then following the conventional process of pad, dry, and cure. In this case the solution is highly acidic from the start, and polymer formation begins immediately. Wrinkle recovery angles of about 260° up to 300° are obtained with 6–10% add-on.

When methylolmelamine is applied to cotton by conventional procedures the material shows a decrease in the infrared absorption band at 2.92 μ (OH). With freshly prepared formic acid colloids of methylolmelamine, less change in the 2.92 μ absorption band is noted with the same add-on of compound. This indicates that the resin reinforcement which occurs with acid colloid more than compensates for a decrease in the degree of cross linking. However, this difference in wrinkle recovery may be caused by the fact that the acid colloid technique causes the finish to occur mainly in the outermost portion of the cell wall, whereas in the conventional process the finish occurs fairly uniformly throughout the fiber wall.

Another example where polymer formation seems to improve the finish is with APO. The initial reaction of APO with cellulose is shown here.,



After the initial reaction has taken place, there still exist two aziridinyl rings which are available to react with additional hydroxyl groups to cross link cellulose. The aziridinyl rings could also lead to polymer formation through attack by electrophilic atoms or molecules at the ring nitrogen. APO, then, is capable of both cross-linking of cellulose and polymer formation. Acid catalysts greatly accelerate polymer formation of solutions of APO when heated to about 90° C. In the usual procedure, APO is applied to cotton fabrics by the pad, dry, and cure technique. By this procedure it can be reacted with cotton, without catalyst, to give a limp, highly cross-linked discolored cotton with poor tensile and tearing strength. With a suitable polymerization catalyst, zinc fluoroborate, a fuller fabric is obtained with no discoloration and better tensile and tearing strength. In both cases the treated fabric has a high wet and dry wrinkle recovery angle. The use of the polymerization catalyst also gives the fabric greater dry muss resistance. The improved strength could be accounted for by a reduction in the amount of cross-linking and an increase in the amount of polymerization in the presence of the acid catalyst. The fuller hand and improved muss resistance must be associated with the presence of polymer.

Similarly, the muss resistance and fullness of hand imparted to cotton by carbonyl bisaziridine (CBA) are improved by the addition of zinc fluoroborate to the finishing solution. This compound is closely related to APO with respect to its reactions and type finish obtained on cotton fabric.

Some additional evidence that polymer formation is desirable is indicated in the difference obtained by treating cotton print cloth with pure methylol triazone and with methylol triazone mixed with urea-formaldehyde. Although the methylol triazone alone gives about the same wrinkle resistance as the mixture, the mixture produces fabrics with slightly higher wash-and-wear ratings. Three pure methylol triazones produced fabric with an average AATCC wash-wear rating of 3, whereas the average rating of fabric finished with four triazones containing UF was 4 [16]. UF with the secondary amido group has a greater tendency to polymerize and form thermosetting resins than the methylol triazones. It should be noted that in each case cited above the improvement has been brought about by the formation of highly cross-linked polymers.

Cross-Linking Without Polymer Formation

To illustrate the effects imparted by cross-linking without any polymer formation, the following two examples are cited. Methyl vinyl ketone was reacted with cotton fabric under basic conditions. The activated olefine [6] added to the cotton to form 3-oxo-n-butylcellulose. These side groups were then joined by reaction with carbohydrazide [9]. The reactions are shown below:

$$\text{Cell—OH} + \text{CH}_2{=}\text{CH—C(=O)—CH}_3 \xrightarrow{\text{OH}^-}$$

$$\text{Cell—O—CH}_2\text{CH}_2\text{C(=O)—CH}_3 \xrightarrow{\text{H}_2\text{NHNC(=O)—NHNH}_2}$$

$$\text{Cell—OCH}_2\text{CH}_2\text{C(CH}_3\text{)=NHNC(=O)—NHN=C(CH}_3\text{)—CH}_2\text{CH}_2\text{O—Cell}$$

The second reaction was carried out by immersion of the modified fabric in aqueous solutions of carbohydrazide. The reaction took place under slightly basic and under slightly acidic conditions. The nitrogen introduced was 0.4%, which means that the maximum extent of cross-linking was very low. In all cases the fabrics were insoluble in cuprammonium

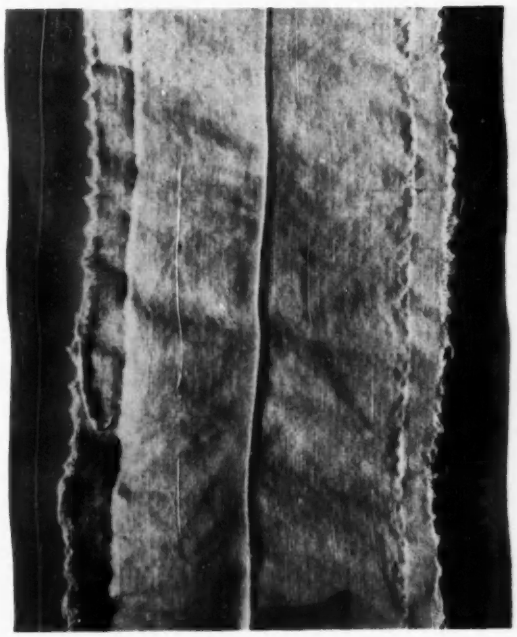
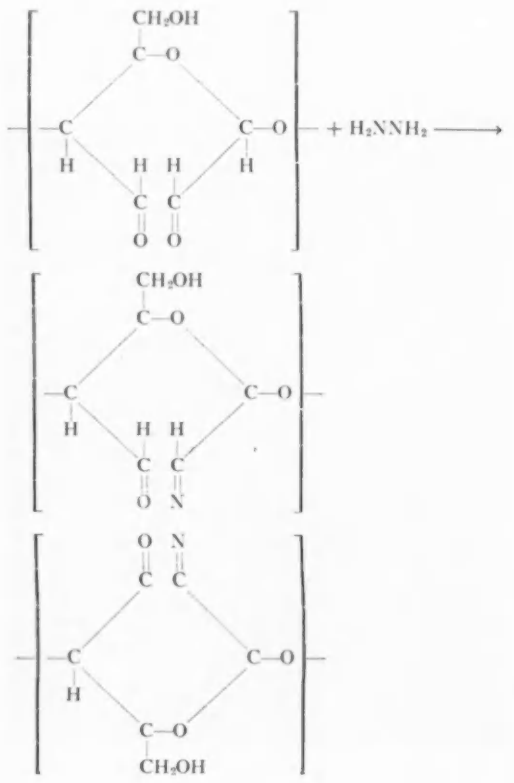


Fig. 2. Fabric with durable crease imparted by pressing while wet with NaOH solution.

solution, indicating that the cellulose molecules were cross-linked. Even with this low degree of cross-linking, the finished fabrics (80 × 80 print cloth) had a dry wrinkle recovery of 245° (W + F) and wet of 205° (W + F). Unmodified control cotton fabric was treated with carbohydrazide under the same conditions described above; detectable amounts of nitrogen were not introduced. This appears to illustrate that polymerization concurrently with cross-linking is not needed to impart wrinkle recovery. It also illustrates that dry as well as wet wrinkle recovery can be imparted by cross-linking while the fabric is immersed in water and in a water-swollen state.

Another good example of cross-linking without polymer formation is with dialdehyde cotton. It is prepared by the selective oxidation of the 2,3 secondary hydroxyl groups with periodic acid. Dialdehyde cotton prepared by this process offers many obvious possibilities for "pure" cross links, some of which have been investigated. One of the possible reactions with hydrazine is indicated here:



Dialdehyde cotton fabric containing up to about 50% dialdehyde—50% of the secondary hydroxyls oxidized—still looks and feels much like unmodified cotton fabric. The fabrics are very sensitive to alkaline solutions, but can be cross-linked with dilute solutions of hydrazine (about 1%) without appreciable damage. Dialdehyde cotton can be cross-linked with more concentrated solutions of carbohydrazine which are less alkaline than hydrazine solutions of the same concentration. Both of these reagents impart wrinkle resistance to the dialdehyde cotton fabric [9]. These reagents do not polymerize under the conditions used here, which consisted of merely immersing the fabric in a dilute aqueous solution of the reagent for a few minutes at about 30° C.

Polymer Formation Alone

Several finishing agents of the cross-linking type have been cured in acetylated cotton to see if resin alone would provide wrinkle resistance and wash-wear properties. The reason for using acetylated cotton was to block the accessible cellulosic hydroxyls which are needed to effect cross-linking of the cellulose. The acetylated cotton print cloth used in these experiments contained 25.6% acetyl. The finishing agents used were urea-formaldehyde precondensate, melamine-formaldehyde precondensate, dimethylolcyclicethyleneurea, formaldehyde, APO, and the formic acid colloid of trimethylolmelamine. The add-on ranged up to about 11%. Many of these, of course, form highly cross-linked polymers. The same cross-linking agents were used on untreated control print cloth. The dry wrinkle recovery angles given in Table I show that the acetylated cotton was not affected. Control print cloth finished with the same chemicals was made highly wrinkle resistant. Wet wrinkle resistance was also determined on some of the acetylated and resin treated fabrics; it was not improved by the finishes.

Secondary Valence Cross Links

In a sense cotton cellulose is essentially a highly cross-linked polymer, cross-linked by hydrogen bonds, and having areas of poor order where the hydrogen bonds are easily broken by water. On wetting, the more easily broken bonds are relaxed; a cotton fabric may be ironed flat and smooth, then creased or pleated. During these processes new bonds are formed which hold the fabric in the desired shape.

Undoubtedly such a dry fabric cross-linked with hydrogen bonds alone would be resistant to mussing and would tend to retain its creases, if it could be kept dry. It has been shown that the wrinkle recovery angle of fabric is increased by thoroughly drying fabric [9]. However, dry cotton is a good desiccant, and there is moisture in the atmosphere. Thus, these improved properties are temporary.

Even after fabric has become hydrated by equilibrating with atmospheric moisture it still has some tendency to maintain its original flat shape. For example, if a narrow strip of cotton fabric is bent just slightly, it will immediately return to its original shape when one end of the strip is freed. If the strip is bent progressively more, soon a point is reached where it will not return to its original shape. At this point the bending force has overcome the weak hydrogen bonds and caused their shifting or redistribution. To secure greater resistance to creasing or mussing either stronger or more cross-linking bonds must be introduced.

The extreme swelling of cotton cellulose in mercerizing strength caustic causes a much greater relaxation of hydrogen bonds than can be obtained with water and permits their re-formation in a desired rearranged form on drying. If an alkali-swollen cotton fabric is pressed with a hot on it can be fixed in either a flat or creased condition [15]. The process can actually impart sharp durable creases and a low degree of wrinkle resistance. This is the result of hydrogen bond cross links. Some of these bonds may be broken by water, but many of them are not broken until the cellulose is reswollen to the initial degree. Smoothness and creases imparted by ironing alkali-swollen cotton are not completely removed by repeated laundering. Thus hydrogen bond cross links may be used to impart some wrinkle resistance and durable creases to cotton fabrics, as shown in Figure 2. The sample shown in this figure has been laundered ten times.

Some Fiber Properties Influenced by Cross-Linking

Relationship of Dry Wrinkle Resistance to Moisture Regain

Dry wrinkle recovery, which is closely related to the extent of cross-linking, is accompanied by a change in moisture regain. This is especially true for fabrics which have been cross-linked by the pad, dry, and cure process. The higher the dry wrinkle recovery, the lower the moisture regain. However, different cross-linking agents applied by the pad, dry, and cure technique to give the same degree of wrinkle resistance may produce fabrics with somewhat different moisture regain. Several factors (for example, the hydrophobicity of the cross-linking agent and the actual extent of cross-linking) may account for differences. Figure 3 shows the general inverse relationship of dry wrinkle recovery (W + F) to moisture regain. Six of the seventeen points used to develop the curve were obtained from fabric finished with dimethylolethyleneurea, three were obtained from fabric finished with commercial triazones, and one was obtained with each of the following

TABLE I. Cross-Linking Finishes on Acetylated Print Cloth

Finishing agent	Non-acetylated control fabric		Acetylated fabric, 25.6% acetyl	
	Weight add-on, %	WRA, W + F	Weight add-on, %	WRA, W + F
None	0.0	171	0.0	138
UF	10.8	302	11.0	124
MF	6.2	268	5.8	124
Formic acid colloid of MF	6.0	280	5.8	145
DMEU	3.6	275	1.5	146
Formaldehyde	0.9	279	0.0	160
APO	8.0	290	7.8	136

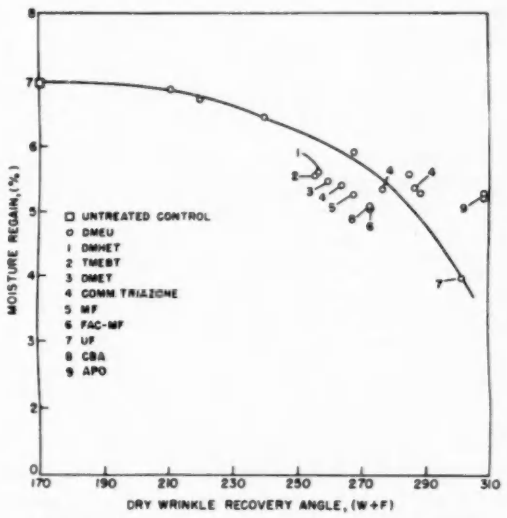


Fig. 3. Influence of dry wrinkle recovery upon moisture regain of cotton fabric.

compounds: dimethylolethyltriazone (DMET), dimethylol hydroxyethyl triazone (DMHET), and tetramethylol ethylene bis triazone (TMEBT). A urea formaldehyde (UF), carbonyl bisaziridine (CBA), tris(1-aziridine)phosphine oxide (APO), a melamine formaldehyde precondensate (MF), and a freshly prepared formic acid colloid of the melamine formaldehyde precondensate (FAC-MF) were used to obtain the other five points. Scoured and bleached print cloth (80 × 80) was used for all of the finishes and as control fabric. Wrinkle resistance varied from 211° where 0.5% DMEU was applied up to the 302° obtained with UF.

Wet wrinkle recovery is not necessarily associated with a decrease in moisture regain. Often fabrics with wet but no dry wrinkle recovery show a substantial increase in moisture regain. Fabric cross-linked with glycerol dichlorohydrin in the alkali-swollen state had a regain value of 9.5%. Yet, fabrics with both wet and dry wrinkle recovery generally have reduced regains. However, the factor which greatly influences the moisture regain of cross-linked cotton is the state of fiber swelling that exists at the time of cross-linking.

Permanent Set

Native cotton fiber will stretch when a force is applied, but the cellulose molecule is relatively inextensible. Stretching of the fiber results in a relative movement of the microscopic and submicroscopic elements [4]. When the stretching force is great enough, some of the structural elements slip into new positions and will not return to their original relative position when the force is relaxed. The resulting distortion is permanent set. On the other hand, if the structural elements are joined by primary valence bonds instead of van der Waals forces or hydrogen bonds, the elements will tend to return to their original relative position when a stretching force is relaxed. Therefore, cross-linking will reduce permanent set. This reduction in permanent set is illustrated in Figure 4. One-inch strips of untreated and DMEU-treated print cloth were put under an 8-Kg. load in the Instron tester and the amount of

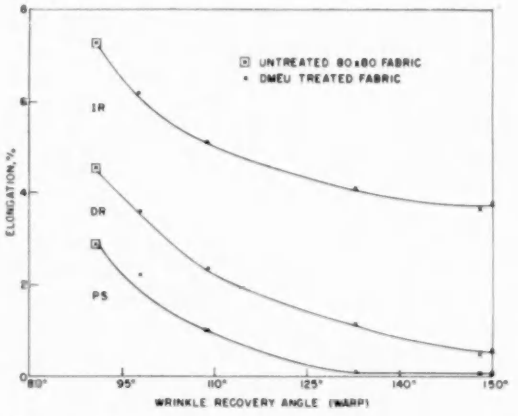


Fig. 4. Influence of dry wrinkle recovery upon permanent set (PS), delayed recovery (DR), and immediate recovery (IR).

TABLE II. Density of Cross-Linked Cotton Fabrics

Cross-linking agent	Catalyst	Reaction conditions	Weight gain, %	Density, g./cc.	Wrinkle resistance	
					Dry W + F	Wet W + F
None	—	—	—	1.545	175	160
Glyceroldichlorohydrin	20% NaOH solution	Solution	<2.0	1.525	173	253
None	20% NaOH solution	Solution	0.0	1.532	187	220
DMEU	$Zn(NO_3)_2$	Oven cure	6.3	1.534	285	280
APO	$Zn(BF_4)_2$	Oven cure	8	1.529	277	247
HCHO	$Zn(NO_3)_2$	Oven cure	—	1.542	237	213
HCHO	HCl	Solution	—	1.541	235	259
Formic acid colloid of trimethylolmelamine	—	Oven cure	7.0	1.543	273	254

elongation was measured. The load was removed and the elongation was measured. The amount of elongation recovered in approximately 30 sec. is termed immediate elastic recovery. The recovery of elongation during the next hour is termed delayed recovery. The elongation still remaining in the fabric after 1 hr. is termed permanent set. It can be seen that untreated cotton fabric has considerable permanent set. The permanent set of DMEU-treated fabric decreases as the wrinkle recovery angle of the fabric increases until there is little or no permanent set.

Density of Cross-Linked Cotton

The density of cotton fiber was altered by all of the types of cross-linking agents examined. Density is a useful criterion of the extent of "openness" of cotton cellulose. Since the density of cross-linked cotton is seldom if ever increased in derivative formation, the native cotton can be referred to as in a collapsed condition and modified cotton can be related to this standard.

Density was determined by the gradient column as used by Orr [13]. Steele has used the gradient column to measure the density of cotton and rayon fabrics finished with urea-formaldehyde type cross-linking agents. Each of these decreased the density [21].

The density of a cross-linked fiber is dependent upon the state of fiber swelling at the time the cross links are established and upon the nature of the reactive compound. Cross-linking with glycerol dichlorohydrin in the presence of mercerizing strength caustic fixes the fiber in a rather open structure; a density of 1.525 g./cc. was obtained as compared to 1.545 for native cotton fiber. Mercerization alone, however, reduced the density to 1.532, as shown in Table II. From these two values it can be seen that the cross links fix or hold the fiber in a more open structure. Cotton cellulose was cross-linked with formaldehyde under essentially dry conditions using zinc nitrate as catalyst in the pad and oven cure technique. In this case the fiber was fixed in essentially a collapsed condition. Fabric was also cross-linked with formaldehyde by immersing it in an aqueous solution of formaldehyde and hydrochloric acid. The reaction was allowed to proceed for 30 min. at about 27° C. Cross-linking in the wet state again produced a slightly more open structure. It is interesting to note that APO fixed the fibers in a highly swollen state. It was applied by the pad, dry, and cure technique using zinc fluoroborate as the catalyst. The formic acid colloid of trimethylolmelamine applied according to Berard, et al. [1] fixed the fiber in a much more collapsed condition.

Before density measurements were made on cross-linked cotton it was assumed that cross-linking finishes that fix the fibers in a swelled condition imparted wet wrinkle resistance and little or no dry wrinkle resistance. It was also assumed that agents which fix the fibers in a collapsed condition imparted dry wrinkle resistance with some wet resistance. However, fabric reacted with dichlorohydrin in mercerizing strength caustic solution has only wet wrinkle resistance, while APO-finished fabric with almost as low density has excellent dry and wet wrinkle resistance. Acid colloid-finished fabric, which is in a collapsed condition, has both wet and dry wrinkle resistance. One relationship that appears to hold is that fabrics cross-linked while highly swollen invariably have wet wrinkle resistance.

Summary

The N-methylol type cross-linking agents are used extensively in the production of minimum-care goods even though they lack good durability, especially to laundering. The reverse hydrolysis reaction is responsible for most of the deficiencies of these compounds. Several other types of compounds in commercial use and being studied in the laboratory also have faults. APO, a compound presently being commercialized, causes white fabrics to yellow when bleached and ironed. However, this compound should be excellent for producing extremely durable minimum-care colored goods. Additional research must be done to find either the ideal cross-linking agent for cotton cellulose or the proper technique of application of existing agents.

Cross-linking agents are very effective in producing changes in the physical properties of the cotton fiber. These changes, especially changes in wrinkle recovery, can be brought about by compounds that cross link the cellulose without self-polymerization. Polymerization reactions that lead to thermosetting resins concurrently with cross-linking of the cellulose do not improve wrinkle recovery angles but may improve some related properties that result in better minimum-care fabrics. Polymer formation without cross-linking of the cellulose does not improve the wrinkle recovery angle. The cross links referred to

above are produced with primary covalent bonds. The value of cross links produced with secondary valence bonds should not be overlooked, because durable physical changes can be produced with these also. For example, a crease held in position by these secondary forces withstood ten launderings.

The moisture regain of cross-linked cotton fabric, produced by the usual pad, dry, and cure technique, which fixes the fibers in a relatively collapsed condition, is inversely related to the dry wrinkle recovery angle, which is a function of extent of cross-linking. Permanent set or the lack of ability of the structural elements of the fiber to slip when a force is applied is directly related to the dry wrinkle recovery. All of the cross-linking agents studied invariably decreased the cotton fiber density. Some caused much greater decreases than others. The cross-linking agents effectively "prop open" the fiber structure, and the extent of this openness is dependent largely upon the extent of fiber swelling at the time of cross-linking.

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Studies of the Surface Geometry of Fibers

Part I: Preliminary Experiments

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Abstract

The background for a study of surface geometry, among other surface properties of fibers, is briefly surveyed. By the adaptation of an instrument designed for measurements in the metals industry, exploratory trials were conducted on specimens of a number of fiber types. Only ranges of readings of "arithmetic average roughness," rather than discrete values, were obtainable, but these results were promising in showing that widely different fiber types—viscose rayon, wool, and raw silk—occupied distinct levels. Indications were that the directional character of the scales on wool fibers could be detected. Further experimentation, still of an exploratory nature, was conducted with refined equipment providing means for graphically recording the irregularities of fiber surfaces. Comparison of tracings obtained in three successive measurements on a single specimen of viscose rayon shows that the tracings are characteristic of the fiber surface and not merely records of extraneous "noise."

Introduction

The behavior of yarns and fabrics in processing, and the performance of the end-product in service, are recognized as depending in no small degree on the properties of the surfaces of the component fibers. Friction and static electrification are two fiber surface properties that have received considerable study.[1] Another fiber property of obvious importance is the surface geometry—the "roughness" or irregularity pattern. Methods have been developed, and tentatively standardized, for the measurement of the irregularity or unevenness of linear textile assemblies [1, 6]. The property in which irregularity is measured by these methods, however, is linear density rather than geometrical contour. Standard methods have been developed for the evaluation of the surface roughness, in the latter sense, of hard solids, principally metals [2].

Heretofore, the only techniques that have been applied to the study of the geometry of fiber surfaces have been optical and electron microscopy [5]. These methods, while yielding much more information than an estimate of fiber contour, are limited to the examination of such minute regions of the specimens that any wide sampling becomes prohibitively tedious. It was thought desirable to develop a technique which would overcome this deficiency and provide a record or numerical data characterizing the surface geometry of an adequate fiber sample. Such data would be of interest in connection with and might bear a relation to the frictional or electrostatic properties of fibers.

[1] Extensive bibliographies are given on friction in textiles [3] and on static electrification [4] in the literature.

Experimental Techniques

It was believed that a tactile method of scanning or surveying a fiber surface offered the most promise. With such a method the objectives mentioned above appeared to be within reach, and it would have the advantage, presumably, of being capable of detecting irregularities in transparent coatings on fibers, which might be invisible with optical techniques.

The initial experiments on textile fibers were performed with an instrument designed in the General Motors Research Laboratories [7] for the measurement of the roughness of machined surfaces in terms of accepted standards [2]. In the intended use of the instrument the probe or pickup, containing an electronic transducer, is moved at constant speed across the surface being analyzed. A stylus, mechanically connected to the transducer, follows the surface irregularities. The resultant motion of the stylus, relative to riders, which carry the pickup over

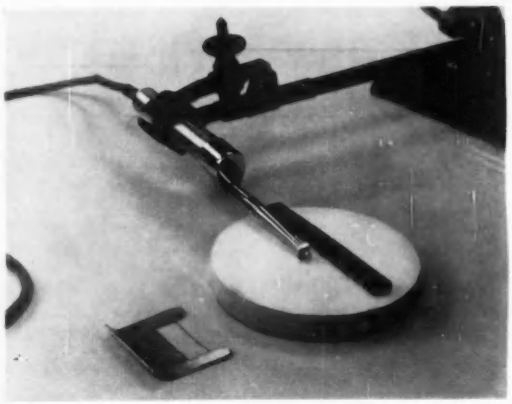

Fig. 1. Pickup and fiber holder used in initial experiments.

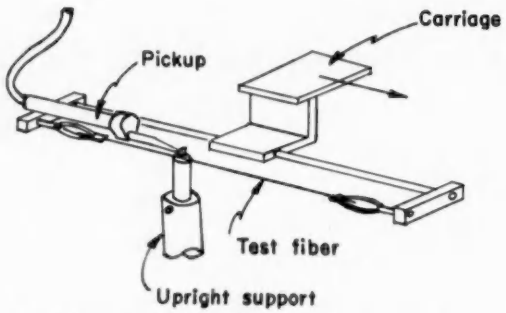

Fig. 2. Schematic drawing of essential features of power-driven instrument for fiber-surface measurements

what corresponds to a "mean" surface, produces continuous variations in a signal voltage. These variations, amplified and treated as an a.c. voltage, produce on a pointer-and-dial meter a relatively stable reading characterizing the particular surface, if the latter is sufficiently uniform. The electromechanical linkage and electronic circuitry of the instrument are designed to yield a measure of the "arithmetic average roughness," according to standardized difinition.[2]

For use in the present exploratory work on textile fibers, the pickup was equipped with an adapter (Brush Model BL-130) having a chisel-shaped stylus, which replaced the regular conical stylus as the surface-probing element. With this type of stylus, having a width of 0.067 in. and an edge of 0.005-in. radius, no trouble was anticipated in keeping it on the test fiber.

With the cylindrical case of the pickup held in a laboratory clamp, the stylus was brought down into near contact with a plated metal disc, as shown in Figure 1. The test fiber was mounted with cement across the opening of a yoke fashioned from sheet brass. Measurements were made by placing the fiber beneath the stylus, bringing the latter down on the fiber, with minimal pressure, and manually passing the fiber lengthwise between the stylus and disc base. The ends of the yoke were held against and slid along a brass strip fixed to the surface of the disc. The strip thus served as a guide to keep the fiber under the stylus.

[2] The commercial instrument, known as the "Surfindicator," Model BL-110, is manufactured by Brush Electronics Company.

Meter readings of "average roughness"[3] on three types of fibers were obtained in this manner. A viscose tire-cord fiber was found to give readings lying in the range 2–8 μin. It was expected that, because of its scaled surface, a wool fiber would show a greater roughness than a viscose sample. This was borne out in measurements made on a washed Buenos Aires Fleece wool fiber, for which, with the fiber moved in one direction, the meter gave readings in the range of 30–40 μin. It was speculated that the differential directional effect in the friction of wool fibers, ascribed to the scaly structure, might be reflected in greater apparent roughness in one direction than in the other. To determine whether the instrument could detect such a difference, the wool fiber was passed under the stylus in the opposite direction. In these experiments readings in the range above 40 μin. were obtained. Measurements on a raw multifilament silk sample gave values in the range 85–110 μin.

These results, in showing distinct levels in surface roughness, or a related property, among different fiber types, and in apparently detecting the directional effect in a wool fiber, were considered sufficiently promising to warrant attempts at further refinement of the technique. It became apparent, however, that with this instrument it was not likely to be possible to obtain on the meter dial a discrete reading, or number, characterizing a particular fiber surface. The pointer was found invariably to move in random fashion over a range of the scale during the traverse of the specimen beneath the stylus. The irregular motion of the pointer was such that not

[3] The average roughness is the arithmetic mean, in a given profile distance, of the heights and depths (without regard to sign) of the surface irregularities, as measured from a hypothetical or nominal mean plane.[2]

even a reliable average value could be deduced from observation of this motion.

Accordingly, it was concluded that means for obtaining a graphic record characteristic of the fiber surface should be provided. For this purpose a chart recorder having a low response time was available. This was used in connection with a matching amplifier [4] and a special input circuit between the pickup and amplifier.

At the same time the decision was reached to build an electrically-driven instrument to pass the test fiber beneath the stylus of the pickup. The essential features are shown schematically in Figure 2. The test fiber, passing between the stylus and top face of an upright steel member, is held in clamps affixed to a traveling carriage. The carriage, running on roller bearings, is driven through a continuous fine cable connected to a rotating drum. The drum, in turn, is driven by a synchronous clock motor. The parameters of the movement are such that the speed of traverse of the fiber across the stylus is 0.13 in./sec. A photograph of the complete instrument, assembled with the recording system, is shown in Figure 3.

With this equipment, tracings were obtained for a number of fiber types. Typical charts for a viscose rayon fiber are shown in Figure 4. The tracings obtained with this type of instrumentaton are not true profiles (enlarged or expanded) of the fiber surface. Because of the principle on which the transducer operates and the characteristics of the electronic circuit, the amplitude of deflection on the tracing represents not solely the height of an irregularity on the fiber surface but also the abruptness

[4] Brush Oscillograph, Model BL-212, and A.C. Amplifier Model BL-905.

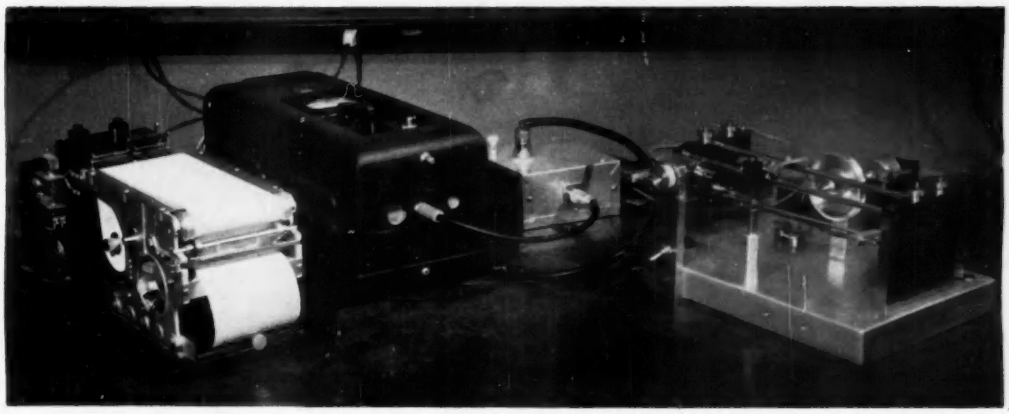

Fig. 3. Surface-measurement instrument assembled with auxiliary electronic recording equipment.

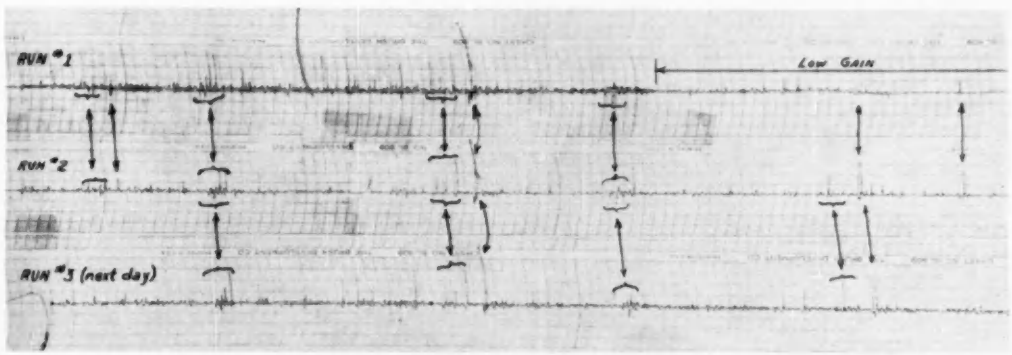

Fig. 4. Chart records of the surface of a single specimen of viscose rayon, showing the replication of prominent features of the tracing.

(slope) with which the irregularity occurs. While a true profile would perhaps be preferable, being more easily interpretable, it was believed that the cumulative signal produced by this type of system, whether recorded graphically or otherwise, would be informatively representative of the irregularity of a fiber surface.

That the tracings obtained are truly characteristic of the surface of a particular fiber specimen, and not merely the result of extraneous noise or the independent random excursions of the stylus, is demonstrated by the charts shown in Figure 4. Three records were obtained on the same specimen of viscose rayon. It can readily be seen, as is indicated in the figure, that many if not most of the prominent features of the tracing are reproduced a second and third time. So far as the small-amplitude signals permit discrimination, inspection of the charts fails to disclose that these signals are reproduced. Hence, it appears likely that there is on the records a sensible but negligible noise component, some of which may have arisen from the motion of the carriage. The instrument had been built on a heavy steel base to minimize this effect.

Discussion

The preliminary research, described in the foregoing paragraphs, established the feasibility of studying fiber surfaces to characterize their geometry quantitatively. It was recognized that the charts in themselves would not accomplish this, except in the case of gross differences in surface character, and that either techniques would have to be developed for the quantitative interpretation of the tracings or further instrumentation undertaken so as to provide means of recording numerical values for a limited array of parameters characterizing a sample fiber surface. Developments in this phase of the study, which followed the latter path, are to be described in Part II.

Acknowledgment

The author is happy to acknowledge the contributions of Harold Lambert to this study in performing most of the design and the construction of the fiber-carriage instrument and the special auxiliary electronic equipment.

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Application of Microscopical Techniques to the Evaluation of Experimental Fibers[1]

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Abstract

Three experimental acrylic fibers were characterized by a variety of microscopical methods and by microradiography in order to correlate their microstructures with measured physical properties and to help explain certain test results. By establishment of a relationship of optical appearances to physical properties for these fibers, future experimental fibers of similar composition could be evaluated and their behavior predicted by comparatively rapid optical methods.

Introduction

The main objective of this article is to demonstrate how an integrated microscopical examination can provide valuable information for fiber technologists and how various techniques of light microscopy, electron microscopy, and microradiography may be used to complement one another. Frequently, too much reliance is placed on one optical instrument alone. The complex nature of most synthetic fibers demands evaluation of the macroscopic appearance as well as that of the ultrastructure. To accomplish this, low and high power light microscopical methods should be used in conjunction with the higher resolving power, but limited field of view, of the electron microscope. Microscopical determination of the optical properties of fibers is also a necessary requisite for a better understanding of fiber behavior; however, this study will deal almost entirely with the microscopical appearance of different fiber textures. Microscopical appearance was correlated with physical properties of the fibers to establish standards by which the textural properties alone could be used to estimate the potential physical behavior of future experimental fibers made from similar polymeric compositions.

Physical Properties of the Fibers

The fibers examined for this paper were of the acrylic type and were especially prepared at the Stamford Laboratories. They are to be considered only as experimental fibers and for obvious reasons details of fiber preparation cannot be discussed. However, some physical measurement data on the three samples can be presented and are shown in Table I. These data show that the fibers have significantly different physical properties. The values shown here are average values obtained from measurements made on at least 30 individual fibers tested at standard conditions of 73° F. and 50% RH. Stress–strain curves in Figure 1 show some of these differences graphically.

Surface area measurements of the bulk fibers were calculated from nitrogen sorption data and represent equilibrium conditions except in the case of Sample B, which failed to attain equilibrium even after long exposure to nitrogen. These data were determined by the BET method [2].

Bundles of these fibers were dyed in a direct dye, Cyanamid's Calcosyn[3] Blue G, to differentiate the samples. Fibers from Sample A, having the high surface area of 65 m.²/g., picked up a considerable

[1] Presented at a meeting of the Polymer and Fiber Microscopy Society held at Textile Research Institute, September 25–26, 1959.

[2] Present address: Esso Research and Engineering Company, Linden, New Jersey.

[3] Trademark of American Cyanamid Company.

TABLE I. Physical Measurement of Fibers A, B, and C

Sample	Surface area, m.²/g.	Yield strength, g./den. at ca. 2.5% elongation	Tenacity, g./den.	Fiber density
A	65.0	1.45	3.6	.83
B	0.7*	.90	2.2	.94
C	0.18	1.35	3.3	1.09

* Sample failed to attain equilibrium.

amount of dye. Fibers from Sample B (0.7 m.²/g.) and Sample C (0.18 m.²/g.) did not pick up visible amounts of dye. Because of its greater surface area, Sample B was expected to have a higher dye pickup than Sample C. This unexpected response of Sample B in the dye bath was explained by further defining its structure microscopically.

Microscopical Examination

Longitudinal Examination by Light Microscopy

As recommended for all microscopical investigations, the first examination was performed at low magnification using the stereoscopic microscope. When viewed by reflected light, the fibers showed marked differences in reflectivity, as illustrated in Figure 2. Sample A was grey-blue, indicating moderate scattering of light. Sample B appeared white, due to strong scattering of light, whereas Sample C appeared glassy and scattered very little light. These variations gave some clue as to continuity of structure. In general, the more discontinuous or complex the structure, the greater the scatter. The high scatter of Sample B indicated a complex structure not revealed by the dyeing procedure.

At higher magnification (150×) in the metallograph, with dark-field reflected illumination, as shown in Figure 3, individual filaments of the three samples exhibited comparable differences to those shown macroscopically in Figure 2. The behavior of Samples A and C with respect to light scattering is consistent with the surface area measurements, which indicated a porous structure for Sample A and a compact structure for Sample C. The extremely strong scattering of Sample B again suggests a discontinuous, complex structure.

Confirmation of the complex structure in Sample B was demonstrated by comparison of the three

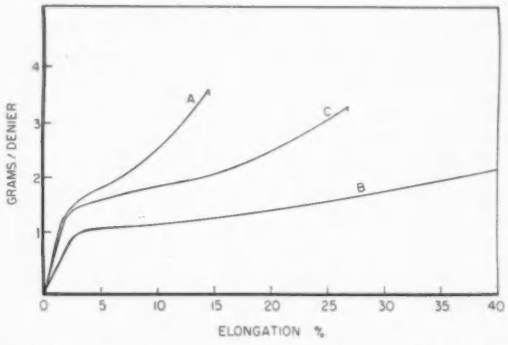

Fig. 1. Stress–strain curves for Fibers A, B, and C.

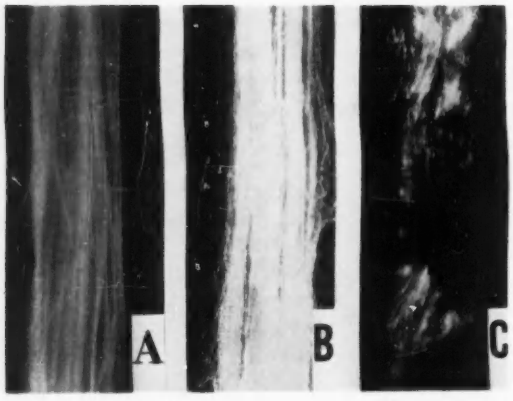

Fig. 2. Macroscopic appearance of Fibers A, B, and C by reflected light, showing distinct differences in reflectivity.

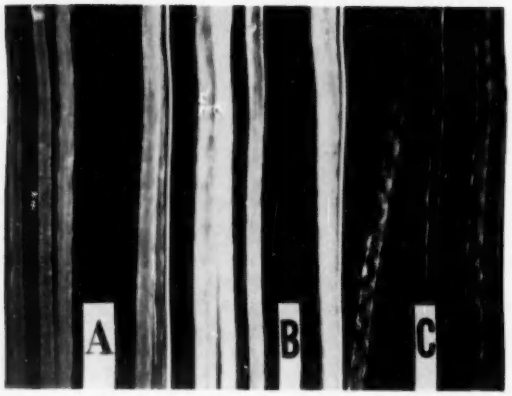

Fig. 3. Photomicrograph of Fibers A, B, and C as viewed by reflected dark-field illumination, showing differences in scattering of light (80×).

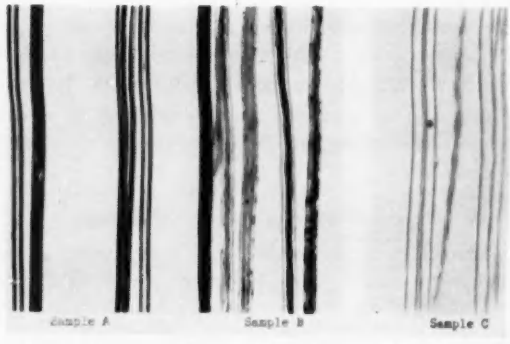

Fig. 4. Fibers A, B, and C immediately after immersion in Nujol mineral oil viewed by transmitted bright-field illumination (compare with Figure 5).

samples with transmitted bright-field illumination, with Nujol mineral oil as a mounting medium. To avoid sealing the fiber ends, the filaments were cut on a piece of cork using a cleaned new razor. Figure 4 clearly shows a skin–core structure for Sample B. Variations in the transmission of light through the specimen indicate a bright, compact skin and a dull, porous core. After several hours of immersion in the Nujol mineral oil, the porous nature of A and the high degree of compactness of C became evident, as shown in Figure 5. Sample A became almost transparent, due to penetration of oil into the pores of the fiber, whereas C remained unchanged in appearance, since its compact structure prevented penetration of the oil. Sample B also remained unchanged, indicating that the skin was very compact. This helps to explain the low dye pickup of Sample B and also explains why this sample failed to attain rapid equilibrium in the nitrogen sorption study.

The three samples were also examined in polarized light. Different ranges of interference colors were noted for each sample. Sample A showed high first-order colors extending into the second-order, Sample B showed medium first-order colors, and Sample C showed only low first-order greys. Since the fibers were of the same composition and thickness, the different ranges of interference colors indicated different constructions.

By itself, the polarized microscope with wave plates inserted does not indicate the degree of porosity intrinsically associated with these different fibers. However, the method does show varying degrees of fiber orientation and construction which are of utmost importance in fiber processing and which are mentioned here only in a cursory way. Structural differences in gross samples of these three fiber types were readily distinguishable by means of a stereoscopic microscope equipped with crossed polaroid sheets. A rotating-polarizing attachment, devised by the late Dr. A. F. Kirkpatrick, can be used for this purpose [4].

The longitudinal surfaces of these fibers were also examined light-microscopically by the surface replica method [1]. The method, which was standardized for acrylic type fibers, involves the use of a suitable holder, one-mil polystyrene tape, heat (120° C.), and pressure (5 lb. wt. on a standard microscope slide), as shown schematically in Figure 6. The soft-iron channel and top plate hold the assembly firmly together and provide for more uniform heating. After removal of the fibers, the negative replica was shadowed with aluminum at an angle of 45° along the fiber axis to enhance detail. The results are shown in Figure 7. The surface of Sample A (porous) was pitted and had relatively few striations. Pits naturally appear as bumps in a negative replica. Sample B (skin–core) had less surface pitting, but had deeper striations. Sample C (compact) had practically no pits but had numerous and still deeper striations.

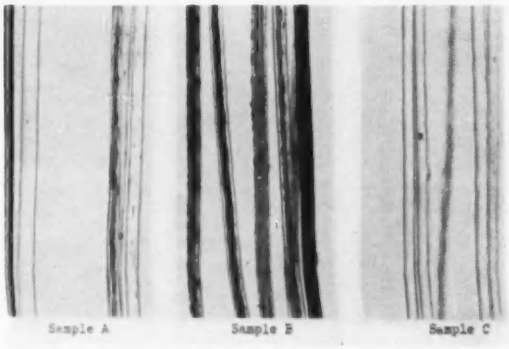

Fig. 5. Fibers A, B, and C after several hours of immersion in Nujol mineral oil showing change in A due to penetration of oil into pores of the fiber—no change in B and C (70×).

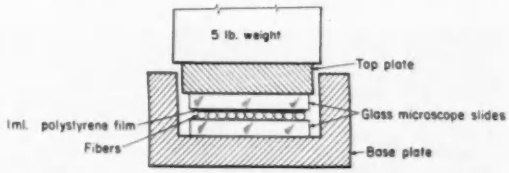

Fig. 6. Cross section of low-pressure press used for forming negative polystyrene replicas (not to scale).

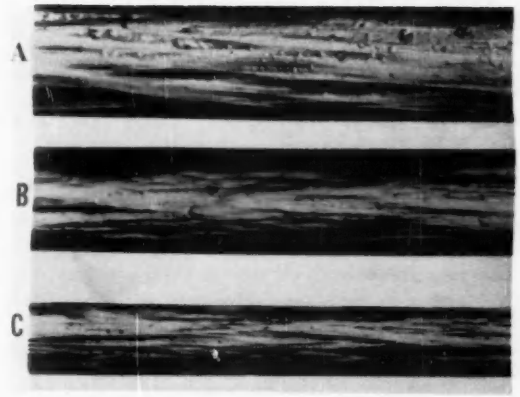

Fig. 7. Negative surface replicas of Fibers A, B, and C viewed light-microscopically by bright-field reflected illumination (900×).

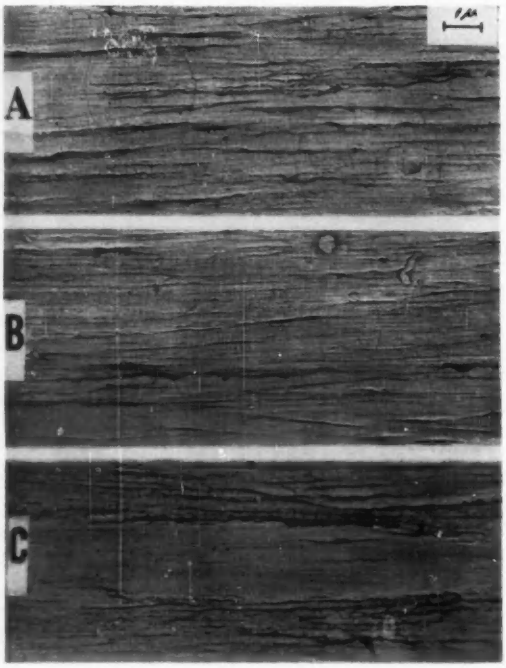

Fig. 8. Electron micrographs of positive replicas of surfaces of Fibers A, B, and C showing fine grain in Fiber A and striation evolvement (6000×).

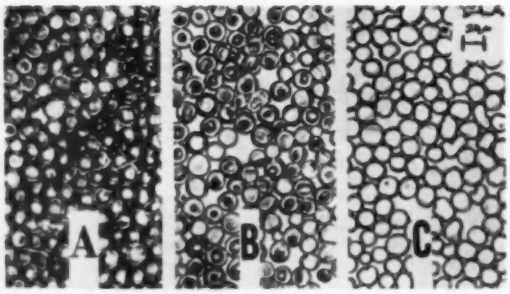

Fig. 9. Light microscopical appearance of Fibers A, B, and C viewed as Hardy cross sections (130×).

Longitudinal Examination by Electron Microscopy

Figure 8 is an electron micrograph of positive silica replicas of surfaces of the three fiber types and confirms the variations shown light-microscopically. Variations in striation evolvement are again visible. Occasional pits or bumps are visible in A and B but do not appear as numerous as in the photomicrographs because of the limited field of view, which measures only about 13 μ in maximum dimension in the electron micrographs. The porous fiber, Sample A, has fine grains, about 100 Å in size, scattered over the surface, whereas the surfaces of B and C, except for the striae, are relatively smooth and continuous.

Cross-Sectional Studies by Light Microscopy

Hardy-type sections, 5–15 μ thick, were examined for internal microstructures. In Figure 9, the fiber cross sections of Sample A, viewed by transmitted bright-field illumination, appear relatively dark. Only a part of the entering light is transmitted through the specimen; the rest is either scattered or absorbed by the porous texture. The complex skin–core structure of Sample B is represented by concentric bright and dull circular bands. The bright bands correspond to compact areas within the fiber and transmit most of the light, whereas the dull areas correspond to porous zones. The cross-sections of fibers in Sample C appear bright. Most of the light is transmitted, indicating a compact structure.

Cross-Sectional Studies by Electron Microscopy

A more definitive study of the fiber structures was made by examining ultrathin sections with the electron microscope.

The method of embedding these fibers for sectioning was different from that conventionally used [7]. Biological tissue, natural and synthetic fibers, and related materials are usually immersed in monomeric mixtures of butyl and methyl methacrylates which penetrate and harden within the specimen. The specimen is thus impregnated and enclosed in a block of compact resin and is ready to be mounted in the ultramicrotome.

However, because this study involves fibers of varying degrees of porosity, there was considerable concern that polymerization of the monomers *in situ* would set up strains within certain porous fibers, thereby introducing modifications of texture. This assumption led to an evaluation of the conventional monomer method and eventually to the development of another method which was considered more advantageous.

Porous fibers from Sample A were selected as our first test specimens. These were embedded in a 90:10 mixture of butyl methacrylate:methyl methacrylate which was catalyzed with 0.5% benzoyl peroxide and then polymerized at 50° C. for 6–8 hr. Ultrathin sections were cut in the Porter-Blum microtome, using glass knives [8]. The sections were recovered in a trough containing a 75:25 mix-

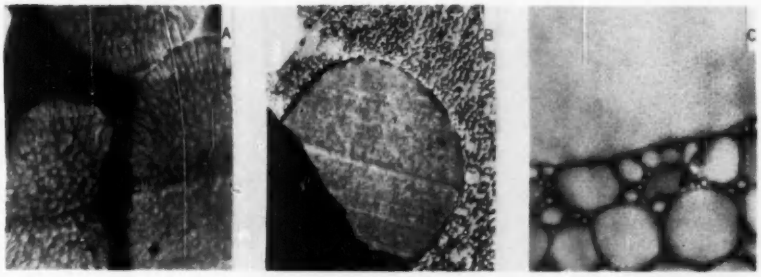

Fig. 10. (A) One-step method, (B) two-step method, (C) latex–methacrylate interface (1500×).

ture of water and acetone in a manner similar to that initially described by Hillier and Gettner [3].

Figure 10A shows that the thin section of the porous fiber (Sample A) embedded by the one-step methacrylate method has a coarse, granular texture resembling a gel. Some differentiation in texture is visible at the periphery. Other textures, characterized by unidirectional lines and fissures, appeared in different sections cut from the same block.

The marked variations in the appearance of these sections suggests that artifacts may have been produced by strong internal stresses generated by polymerization of the monomers within the pores of the fibers.

To prevent distortion due to these internal stresses, another bundle of test fibers from Sample A was selected, but was first precoated in an aqueous suspension of a resin latex. The relatively large latex particles could not penetrate the pores of the fibers and had film-forming properties. Fibers that were dipped in the latex and then air-dried became encased in a tough protective film. The fiber bundle was then further mounted in methacrylate and sectioned in the manner previously described. Figure 10B shows a uniform, fine-grained texture that was highly reproducible. This led to the conclusion that this two-step mounting procedure allows the production of ultrathin sections which more faithfully show the intrinsic nature of the fiber sample. Another advantage of this method is that the coalesced latex matrix, represented by the mottled area surrounding the fiber in Figure 10B, has high thermal stability in an electron beam of moderate intensity. Because the latex does not soften like methacrylate, micrography is simplified.

In the preparation of fibers by the two-step latex-methacrylate method, it was observed that the methacrylate monomer had a slight swelling or solvent action on the dried latex film, as shown in Figure 10C. Undesirable effects from this action can be

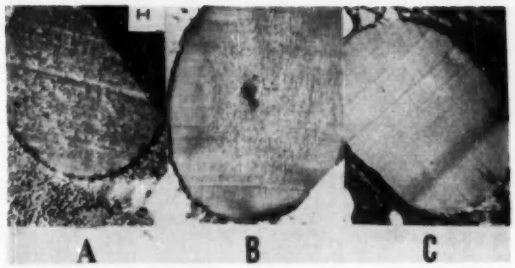

Fig. 11. Ultrathin cross sections of Fibers A, B, and C as viewed in the electron microscope (1400×).

prevented by maintaining proper initial thickness of the latex film and by controlling the rate of polymerization of the methacrylates.

The net results of these efforts has been a more confident interpretation of electron micrographs of ultrathin sections, particularly where porous textures are involved.

Each of the samples had different internal structures, as shown by Figure 11. Sample A appeared generally rough, Sample B had smooth and rough concentric bands, and Sample C appeared generally smooth.

Sectioning with any type of knife involves a shearing action which disturbs the faces of the cut sections. However, there appears to have been very little surface distortion introduced in this particular series of samples; otherwise the concentricity of the porous and compact zones shown in Figure 12 would probably not have been maintained. Another indication of the good quality of the knives is the smooth appearance of the cut methacrylate surface (Figure 10C), which was adjacent to the fiber bundle.

Microradiographic Examination

Radiography and x-ray microscopy have been applied with considerable success to the study of many biological specimens and complex inorganic materials [6]. Thickness gauges based on the measure-

Fig. 12. Electron micrographs of ultrathin sections of Fiber B, showing the relatively undisturbed concentric relationship between compact and porous areas in this skin–core fiber (3500×).

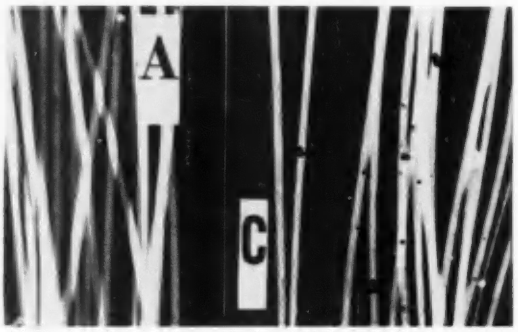

Fig. 13. Microradiograph of Fibers A and C showing variation in x-ray absorption (negative print enlarged to 45×).

ment of β-ray transmission through films and foils are well known [5]. However, there is a dearth of information in the literature concerning the microradiography of fibers.

As part of this comprehensive study of fibers representing extremes in textures, it was therefore decided to apply the radiographic method to determine whether variations in fiber porosity could be correlated with the attenuation of a soft x-ray beam.

Single fibers from Samples A and C (porous and compact fibers, respectively) were mounted side by side and exposed simultaneously to a 2.5 KV x-ray beam at a current of 4 mA for 5 min. in a Philips (CMR-5) microradiographic instrument. Fine-grain film (Kodak 548) was used to record the image, which appears in Figure 13 as an enlarged negative print. The porous fibers at the left appear darker, indicating greater transmission of x-rays than the compact fibers at the right.

Densitometric traces on an enlarged positive transparency of the original x-ray negative were made by

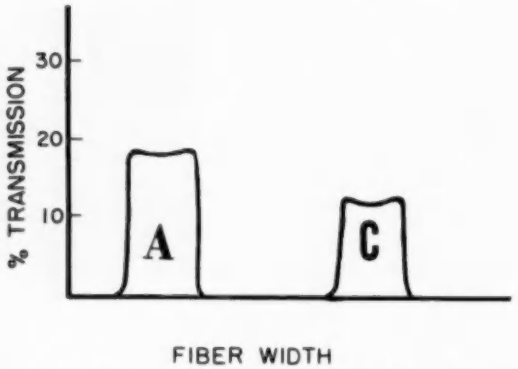

Fig. 14. Graphic representation of densitometric traces on radiographic negatives showing variations in percent transmission in Fibers A and C.

scanning several fibers from each sample with a Leeds and Northrup recording photometer. The area scanned was 0.5 × 1.5 mm. and the scanning rate was 10 mm./min. The densitometric trace, shown graphically in Figure 14, is related to the x-ray transmission through the fiber and to the intrinsic fiber porosity. The porous fiber, Sample A, had an average transmission value of 18.8%, whereas the compact fiber, Sample C, gave an average transmission value of only 11.2%. The sensitivity of this method, as applied to quantitative measurement of porosity, still has to be determined. However, the fact that variations in x-ray transmission are detectable in fibers which are only about 20 μ thick is encouraging.

Conclusions

In this paper it has been our intention to show how several microscopical methods may be used to confirm and complement each other in the study of fiber structures and to apply these methods to explain certain anomalous test results. The extent of their use depends on what is specifically being sought. For example, the behavior of the skin–core fiber, when dyed, could not be fully explained until light microscopical methods demonstrated the presence of a compact skin and a relatively porous core. On the other hand, the physical appearance and spatial distribution of porosity in Sample A could not be shown in detail until cross sections and surface replicas were examined with the light and electron microscopes. For the general study of fiber surface detail, the examination of replicas with the light microscope was more expedient.

In a basic study it may be necessary to bring many other methods to bear, in addition to those described above, to demonstrate in convincing detail how the microscopical characteristics of texture, size, shape, and structure are inevitably related to ultimate physical properties.

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Thermodynamic Properties of Dilute Solutions of Cellulose Derivatives

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Abstract

Values of the free energies, heats, and entropies of dilution are given for dilute solutions of cellulose acetates, cellulose nitrate, and ethyl cellulose in representative solvents. In a number of cases heats of dilution are positive and possibly related to the solubility parameter of the solvent. Entropies of dilution are less than those for comparable systems containing less polar, more flexible polymers. Values of the interaction parameter χ_1 and the heat and entropy contributions, χ_h and χ_s, are calculated using the densities of the dry polymers. Some of the values of χ_s appear to be unrealistic. Assumptions are made regarding solvation and the densities and volume fractions of the solvated polymers are estimated and used to obtain values of χ_1, χ_h, and χ_s for interaction between solvated polymer and solvent. Values of χ_s appear to be in better agreement with simpler lattice theories.

Introduction

Cellulose derivatives differ from most other high polymers in polarity and chain stiffness. Their high polarity often leads to solvation, which may be an essential preliminary to solution. Evidence for such specific interaction between polar groups of polymer and solvent has been previously summarized [22] and reviewed [27]. It appears to involve Lewis acid–base interaction or hydrogen bonding [4, 5, 15, 19, 27]. Hydroxyl, nitrate, acetyl, or ether groups of the derivative may be involved [22, 27]. The number of solvent molecules bound to each such group is not certain. Small numbers seem probable, but as many as 7 to 19 per substituted glucose residue have been suggested [6, 30]. Firm binding of large numbers seems unlikely, but attraction may be propagated from a first solvation layer [26]. The solubility of certain ethyl celluloses in nonpolar solvents suggests that solvation may not always be necessary.

The effects of solvation and chain stiffness are shown by variations in thermodynamic properties and parameters of cellulose derivative–solvent systems with concentration. In the cellulose nitrate–acetone system, heats and entropies of dilution are strongly negative at high concentrations of poly-

TABLE I

Derivative	Characteristics	Solvents
Cellulose acetate	$\bar{M}_n$ 104,000. Acetic acid yield 53.7%. d_4^{25} 1.3982	acetone, aniline, methyl acetate, dioxan, pyridine, nitromethane
Cellulose triacetate	$\bar{M}_n$ 166,000. Acetic acid yield 62.5%. d_4^{25} 1.3040	chloroform, methylene chloride, s-tetrachlorethane
Cellulose nitrate	$\bar{M}_n$ 95,000. Nitrogen content 12.5%. d_4^{25} 1.6280	acetone, n-amyl methyl ketone, methyl acetate, n-butyl acetate, nitrobenzene
Ethyl cellulose	$\bar{M}_n$ 112,000. Ethoxyl content 48.1%. d_4^{25} 1.143	acetone, n-amyl methyl ketone, methyl acetate, n-butyl acetate, chloroform, benzene, carbon tetrachloride

mer [26], the solvent molecules being concerned in solvation with evolution of heat. Orientation of solvent causes a reduction in entropy. Heats and entropies decrease as the polymer concentration falls and solvated polymer mixes with solvent. Heats of dilution for some dilute ethyl cellulose–solvent [21] and secondary cellulose acetate–solvent [14, 21] systems are positive and the entropies of dilution, although less than for similar systems involving less polar and more flexible polymers, are also positive and greater than "ideal" values. Values of the interaction parameter χ_1 for cellulose nitrate–solvent systems vary from large negative to small negative or even positive values as the concentration of polymer is reduced [1, 31].

The properties of dilute solutions of cellulose derivatives resemble those of systems containing less polar polymers in a number of ways. The volumes of non-solvents required to cause initial phase separation from solutions of cellulose nitrate, secondary acetate, and ethyl cellulose vary, in a series of solvents of similar type, in a manner similar to that observed with less polar polymers; the variation has been interpreted in a similar way [17, 22]. The intrinsic viscosity also varies with solvent in a somewhat similar way to that for more flexible polymers although, because of chain stiffness, the variation is smaller [16, 22]. These resemblances have been tentatively interpreted in terms of interaction between solvent and solvated polymer, the latter being regarded as effectively nonpolar [22].

In further studies of cellulose derivative–solvent interaction free energies, heats, and entropies of dilution have been obtained for dilute solutions of cellulose acetates, cellulose nitrate, and ethyl cellulose in representative solvents [32]. These are discussed, values of χ_1 and the heat and entropy contributions to χ_1 obtained, and an attempt made to interpret the results in terms of interaction between solvated polymer and solvent.

Experimental

The cellulose derivatives and solvents used are given in Table I. The derivatives were fractions and of similar molecular weights. The incompletely substituted derivatives are of comparable degree of substitution. The triacetate was obtained from the secondary by nondegradative acetylation [11]. Degrees of substitution were obtained by standard methods. Number average molecular weights, $\bar{M}_n$, of the incompletely substituted derivatives were determined osmotically in acetone at 25° ± 0.01°, that of the triacetate being determined similarly in chloroform. Densities were determined in hexane at 25° and 35°. The best available grades of solvents were further purified where necessary, dried with appropriate drying agents, and fractionally distilled just before use.

Values of the free energy, heat, and entropy of dilution of dilute solutions were obtained from values of the osmotic pressure π at 25° ± 0.01° and 35° ± 0.01° C. For dilute solutions, the free energy of dilution, $\Delta\bar{F}_1$, is given by

$$-\Delta\bar{F}_1 = \pi\bar{V}_1 \qquad (1)$$

$\bar{V}_1$, the partial molar volume of the solvent, can be replaced, in dilute solutions, by the molar volume V_1. The heat of dilution, $\Delta\bar{H}_1$, is given by

$$\Delta\bar{H}_1 = \delta(\Delta\bar{F}_1/T)/\delta(1/T) \qquad (2)$$

and the entropy of dilution, $\Delta\bar{S}_1$, by

$$\Delta\bar{S}_1 = \delta\Delta\bar{F}_1/\delta T \qquad (3)$$

where T is the absolute temperature. As a close approximation the differentials may be replaced by differences between values at not too different temperatures so that

$$\Delta\bar{H}_1 = \frac{1/T_1(\pi V_1)_{T_1} - 1/T_2(\pi V_1)_{T_2}}{1/T_2 - 1/T_1} \qquad (4)$$

and

$$\Delta\bar{S}_1 = \frac{(\pi V_1)_{T_1} - (\pi V_1)_{T_2}}{T_1 - T_2} \qquad (5)$$

the values obtained referring to the mean of T_1 and T_2.

Osmotic pressures of dilute solutions in the concentration range 0.2–1.0 g./ml. were determined statically at 25° and 35° and in some cases also at 15° and 45° using Schulz-Wagner type osmometers with denitrated collodion membranes. Temperatures were controlled to 0.01°. In a few cases Pinner-Stabin osmometers with cellophane membranes were also used. No significant differences were observed between results obtained with the two different osmometer–membrane systems. Tests for diffusion were invariably negative. At least two series of measurements were made with each solvent at each concentration and temperature. Reproducibility was good, osmotic heads not differing by more than about 5%. All solutions were

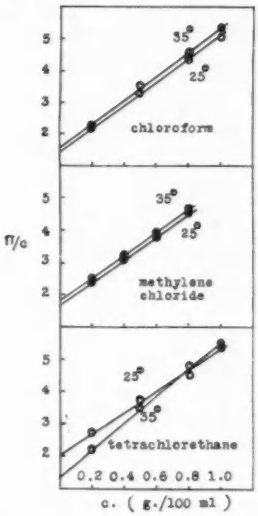

Fig. 2. π/c versus c plots. Cellulose triacetate.

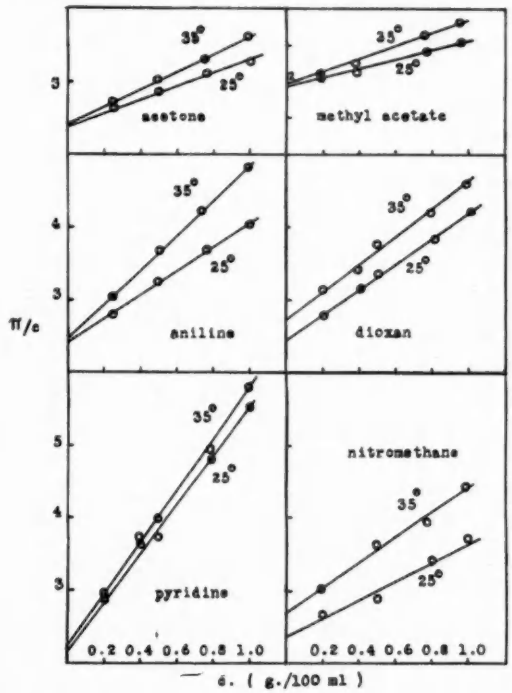

Fig. 1. π/c versus c plots. Secondary cellulose acetate.

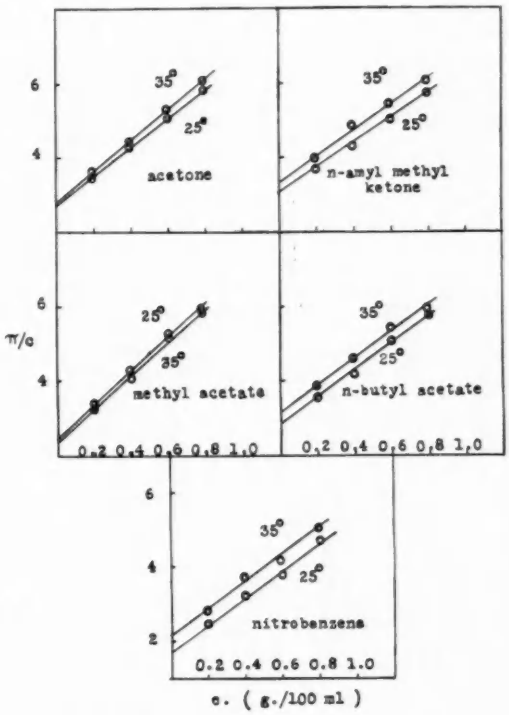

Fig. 3. π/c versus c plots. Cellulose nitrate.

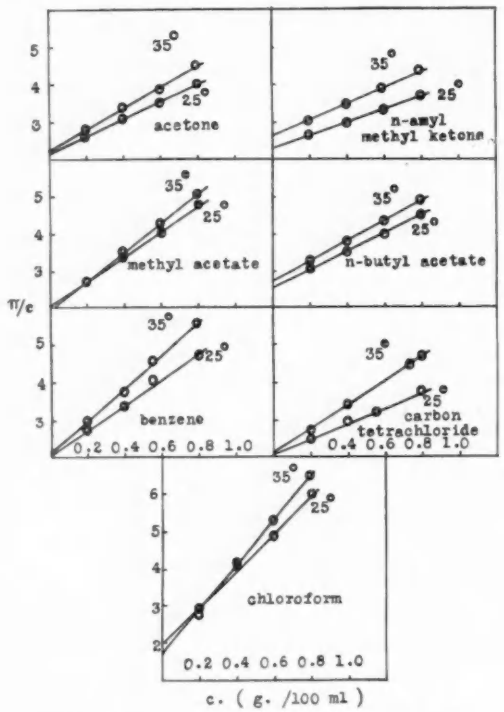

Fig. 4. π/c versus c plots. Ethyl cellulose.

prepared two weeks before use and stored in the dark at room temperature.

Results

Plots of π/c against c, where c is the concentration of polymer, are shown in Figures 1–4. All are linear and were obtained by the method of least squares.

Discussion

Values of $\bar{M}_n$ from

$$\lim_{c \to 0} \pi/c = RT/\bar{M}_n \qquad (6)$$

with an estimated error of not more than 5% are collected in Table II. They show some variation with both solvent and temperature. Differences in the values for each derivative at 25° are, in most cases, probably due to differences in the degree of degradation during storage of solutions. Such degradation, varying with solvent, is well known [28], particularly with cellulose nitrate and ethyl cellulose. In the cases of the secondary acetate in methyl acetate, the nitrate in nitrobenzene, and, perhaps, ethyl cellulose in methyl acetate, chloroform, benzene, and carbon tetrachloride, values at 25° are larger than might be expected from those in other solvents. Association of polymer is possible,

TABLE II. Values of $\bar{M}_n$

Derivative	Solvent	25°	35°
Secondary cellulose acetate	acetone	104,000	105,000
	aniline	105,000	104,000
	methyl acetate	134,000	134,000
	dioxan	102,000	94,000
	pyridine	113,000	113,000
	nitromethane	106,000	98,000
Cellulose triacetate	chloroform	166,000	165,000
	methylene chloride	168,000	162,000
	s-tetrachlorethane	127,000	180,000
Cellulose nitrate	acetone	95,000	95,000
	n-amyl methyl ketone	87,000	77,000
	methyl acetate	102,000	112,000
	n-butyl acetate	90,000	85,000
	nitrobenzene	140,000	124,000
Ethyl cellulose	acetone	112,000	114,000
	n-amyl methyl ketone	111,000	102,000
	methyl acetate	125,000	137,000
	n-butyl acetate	100,000	96,000
	chloroform	125,000	163,000
	benzene	121,000	123,000
	carbon tetrachloride	122,000	125,000

TABLE III. Values of $\Delta\bar{F}_1$, $\Delta\bar{H}_1$, and $T\Delta\bar{S}_1$

Derivative	Solvent	Conc., g./100 ml.	cal./mole × 10^3			
			$-\Delta\bar{F}_1$	$\Delta\bar{H}_1$	$T\Delta\bar{S}_1$	$T\Delta\bar{S}_1$ (ideal)
Secondary cellulose acetate	acetone	0.25	1.15	0.35	1.5	1.1
		0.5	2.5	1.4	3.9	2.15
		0.75	4.2	4.7	8.9	3.2
		1.0	5.9	10.5	16.4	4.3
	aniline	0.25	1.6	3.0	4.6	1.3
		0.5	3.7	10.1	13.8	2.6
		0.75	6.3	25.8	32.1	3.9
		1.0	9.7	37.8	47.6	5.2
	methyl acetate	0.25	1.0	0.8	1.8	0.9
		0.5	2.1	2.5	4.6	1.8
		0.75	3.5	5.6	9.1	2.7
		1.0	5.1	9.0	14.1	3.6
	dioxan	0.25	1.5	0.35	1.85	1.25
		0.5	3.4	1.7	5.1	2.5
		0.75	5.9	3.6	9.5	3.75
		1.0	8.8	4.0	12.8	5.0
	pyridine	0.25	1.5	0.3	1.8	1.4
		0.5	3.7	1.4	5.1	2.9
		0.75	6.9	2.8	9.7	4.3
		1.0	10.7	4.8	15.5	5.7
	nitromethane	0.25	0.9	1.0	1.9	0.8
		0.5	2.1	4.5	6.6	1.5
		0.75	3.7	8.7	12.4	2.3
		1.0	5.2	14.9	20.1	3.0
Cellulose triacetate	chloroform	0.25	1.2	0.9	2.1	0.9
		0.5	3.3	1.3	4.6	1.8
		0.75	6.2	1.6	7.8	2.8
		1.0	9.8	2.3	12.1	3.6
	methylene chloride	0.25	0.9	− 0.4	0.5	0.6
		0.5	2.5	− 1.3	1.2	1.2
		0.75	5.0	− 2.6	2.4	1.8
		1.0	7.8	− 3.6	4.2	2.4
	s-tetrachlorethane	0.25	1.2	− 8.5	− 7.3	1.15
		0.5	4.1	−12.2	− 8.2	2.1
		0.75	8.5	−11.2	− 2.7	2.8
		1.0	13.7	− 5.8	7.9	3.5
Cellulose nitrate	acetone	0.25	1.6	− 0.6	1.0	1.2
		0.5	4.2	− 1.1	3.1	2.4
		0.75	7.6	− 1.2	6.4	3.6
		1.0	11.8	− 1.2	10.6	4.7
	n-amyl methyl ketone	0.25	3.2	− 1.9	1.3	2.45
		0.5	7.8	− 3.9	3.9	4.9
		0.75	14.0	− 8.5	5.5	7.35
		1.0	21.4	−11.4	10.0	9.85
	methyl acetate	0.25	1.7	− 1.7	0.0	1.2
		0.5	4.5	− 3.8	0.7	2.35
		0.75	8.4	− 5.7	2.7	3.55
		1.0	13.3	− 8.1	5.2	4.7

TABLE III.—(*Continued*)

Derivative	Solvent	Conc., g./100 ml.	cal./mole × 10^3			
			$-\Delta\bar{F}_1$	$\Delta\bar{H}_1$	$T\Delta\bar{S}_1$	$T\Delta\bar{S}_1$ (ideal)
	n-butyl acetate	0.25	3.0	0.5	3.5	2.25
		0.5	7.4	− 2.3	5.1	4.5
		0.75	13.2	− 5.9	7.3	6.7
		1.0	20.5	− 9.9	10.6	8.9
	nitrobenzene	0.25	1.7	3.9	5.6	1.55
		0.5	4.6	6.6	11.2	3.1
		0.75	8.6	8.4	17.0	4.65
		1.0	13.8	8.3	22.1	6.2
Ethyl cellulose	acetone	0.25	1.2	0.9	2.1	1.0
		0.5	2.8	4.5	7.3	1.9
		0.75	5.3	10.1	15.4	2.85
		1.0	8.2	18.2	26.4	3.8
	n-amyl methyl ketone	0.25	2.3	2.1	4.4	1.9
		0.5	5.5	8.5	14.0	3.85
		0.75	9.7	17.9	27.6	5.75
		1.0	14.7	31.7	46.4	7.7
	methyl acetate	0.25	1.3	− 2.3	− 1.0	1.0
		0.5	3.5	− 2.1	1.4	1.95
		0.75	6.5	− 1.9	4.6	2.9
		1.0	10.3	0.3	10.6	3.9
	n-butyl acetate	0.25	2.5	1.3	3.8	2.0
		0.5	6.1	5.0	11.1	4.0
		0.75	10.5	9.7	20.2	6.0
		1.0	16.3	19.8	36.1	8.0
	chloroform	0.25	1.5	− 2.2	− 0.7	1.0
		0.5	4.4	2.7	7.1	1.95
		0.75	8.7	15.9	24.6	2.9
		1.0	13.8	36.2	50.0	3.9
Ethyl cellulose	benzene	0.25	1.6	2.8	4.4	1.1
		0.5	4.2	11.8	16.0	2.25
		0.75	7.9	28.1	36.0	3.35
		1.0	12.6	51.6	64.2	4.5
	carbon tetrachloride	0.25	1.6	4.1	5.7	1.2
		0.5	3.9	17.9	21.8	2.45
		0.75	7.1	41.5	48.6	3.65
		1.0	11.0	75.1	86.1	4.9

and the reduction in $\bar{M}_n$ for the nitrate at 35° agrees with this view. A value of 112,000 was obtained at 45°. Association of ethyl cellulose in nonpolar solvents has been reported [29]. The possible association of the secondary acetate in methyl acetate and ethyl cellulose in benzene and carbon tetrachloride would appear to be independent of temperature in the range considered. Similar behavior has been observed with polyvinyl chloride in dioxan [7], but the somewhat higher values of $\bar{M}_n$ may be due to smaller degrees of degradation.

The larger values at 35° for the triacetate in tetrachlorethane, the nitrate and ethyl cellulose in methyl acetate, and ethyl cellulose in chloroform may be due to association and possibly some desolvation at the higher temperature. At 45° the apparent $\bar{M}_n$ for ethyl cellulose in chloroform is 200,000 and the values for ethyl cellulose and the nitrate in methyl acetate at 15° are 116,000 and 98,000 respectively. Similar results have been obtained with polyvinyl acetate–alcohol copolymers [25]. The value of $\bar{M}_n$ for the triacetate in tetrachlorethane at 45° is 160,000, which is less than that at 35°; this system is clearly complex. The results of Hagger and van der Wyck [9] suggest a somewhat similar variation.

Significantly lower values of $\bar{M}_n$ at 35°, seen in some cases, are probably due to greater degradation at this temperature during the period of osmotic measurements. In such cases the observed temperature coefficients of osomotic pressure will be greater than if $\bar{M}_n$ were unaltered and values of $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$, obtained from Equations 4 and 5, will be greater than the correct values. In such cases values of π/c at zero concentration were calculated from those at 25°, assuming no change in $\bar{M}_n$, and the π/c against c plots displaced vertically so as to intercept the ordinate at the calculated values. The slopes of the plots should not vary in the narrow molecular weight range concerned. Values of $\Delta\bar{H}_1$ and $T\Delta\bar{S}_1$ at 30° have been calculated by use of Equations 4 and 5 from osmotic pressures interpolated at equal weight fractions from these plots and those for which $\bar{M}_n$ does not vary significantly with temperature. These are given in Table III, together with values of $\Delta\bar{F}_1$ and "ideal" values of $T\Delta\bar{S}_1$ obtained from

$$\Delta\bar{S}_{1(\text{ideal})} = Rx_2 \qquad (7)$$

where x_2 is the mole fraction of polymer. Values for the systems in which association and other effects are possible are also included. Typical plots showing $\Delta\bar{F}_1$, $\Delta\bar{H}_1$, and $T\Delta\bar{S}_1$ as functions of concentration are shown in Figure 5.

All the secondary acetate systems are endothermal, with entropies of dilution greater than ideal values. Heats and entropies for the acetate–aniline system are larger than in other cases. The ethyl cellulose systems, with the exception of that involving methyl acetate, which is nearly athermal, are also endothermal, and the entropies of dilution are generally larger than those of the other systems. Benzene and carbon tetrachloride are associated with large values of $\Delta\bar{H}_1$ and $T\Delta\bar{S}_1$, the latter approaching those for systems involving flexible, less polar polymers. With the exception of that involving nitrobenzene, the cellulose nitrate systems are exothermal, with entropies of dilution near ideal values. Similar results have been obtained by Schulz [26] and by Boissonas and Meyer [2]. The triacetate–methylene chloride system resembles those for cellulose nitrate, but the triacetate–chloroform system is similar to those of the secondary acetate. The triacetate–tetrachlorethane system is exothermal, with negative entropies of dilution, both $\Delta\bar{H}_1$ and $T\Delta\bar{S}_1$ increasing and then decreasing as the concentration increases.

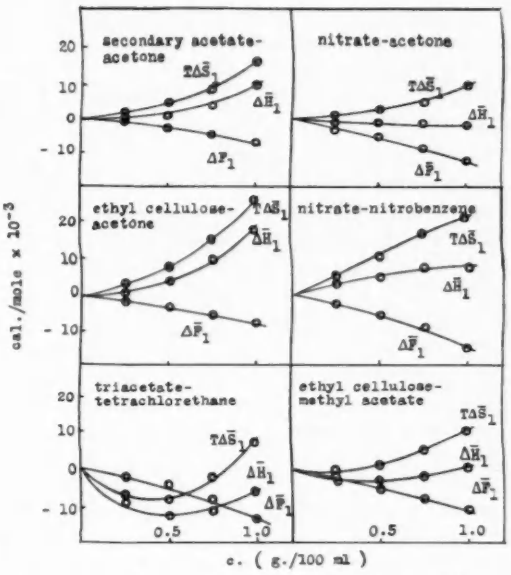

Fig. 5. Typical examples of $\Delta\bar{F}_1$, $\Delta\bar{H}_1$, and $T\Delta\bar{S}_1$ as functions of concentration.

Solvation is likely to be complete or nearly so in the dilute solutions considered. The solvated polymer should be less polar than the unsolvated. Dilution may involve endothermal mixing of solvated polymer and solvent, accounting for the positive values of $\Delta\bar{H}_1$ obtained for the secondary acetate and ethyl cellulose systems. In the case of the more polar nitrate, some propagated attraction may lead to negative values. Munster [24] has suggested that dilution may free solvent clusters which block nitrate groups, leading to further orientation of solvent with evolution of heat and a reduction in $\Delta\bar{S}_1$. The endothermal character and larger values of $\Delta\bar{S}_1$ in the cellulose nitrate–nitrobenzene system might be due to association or a difference in the extent or nature of solvation. Endothermal and exothermal dilution effects may occur together, but to differing extents, and this might account for the endothermal and exothermal natures of the triacetate–chloroform and triacetate–methylene chloride systems respectively. Reasons for the variations of $\Delta\bar{H}_1$ and $T\Delta\bar{S}_1$ with concentration in the triacetate–tetrachlorethane system are not clear. The negative values of $\Delta\bar{H}_1$ and $T\Delta\bar{S}_1$ suggest strong orientation effects, and Hagger and van der Wyck [9] have suggested extensive solvation in this system.

According to Hildebrand and Scott [10], in

cases of endothermal mixing where dispersion forces only are involved

$$\Delta\bar{H}_1 = KV_1(\delta_1 - \delta_p)^2\phi_2^2 \qquad (8)$$

where K is a constant for a particular system, ϕ_2 the volume fraction of polymer, and δ_1 and δ_p the solubility parameters of solvent and solvated polymer. If exothermal effects are absent or small, values of $\Delta\bar{H}_1$ for the endothermal secondary acetate and ethyl cellulose systems might be expected to vary with $V_1(\delta_1 - \delta_p)^2$. δ_p will presumably vary with the solvent, but values of approximately 11.0 and 9.3 at 25° have been suggested for the secondary acetate and ethyl cellulose in polar solvents and a value of 10.0 for ethyl cellulose in nonpolar ones [22]. Figure 6 shows values of $\Delta\bar{H}_1$ for 1% solutions as a function of $V_1(\delta_1 - \delta_p)^2$. The acetate–aniline system is excluded, but with this exception there appears to be a rough proportionality. Better agreement is not to be expected in view of the approximate values of δ_p, the possible contributions of exothermal effects, and variations in K and ϕ_2. Large values of $\Delta\bar{H}_1$ for the acetate–aniline system, which are associated with relatively large values of $\Delta\bar{S}_1$, may be due to some ordering of aniline molecules which is reduced on addition to the solution [20].

Simpler lattice theories [8, 12] predict that $\Delta\bar{H}_1/\phi_2^2$ should be independent of concentration. This does not hold over a wide concentration range for polymers generally, but little variation might be expected in the narrow range considered here.

TABLE IV. Typical Values of $\Delta\bar{H}_1/\phi_2^2$ and $\Delta\bar{S}_1/\phi_2^2$

Derivative	Solvent	Conc., g./100 ml.	cal./mole $\Delta\bar{H}_1/\phi_2^2$	cal./mole $\Delta\bar{S}_1/\phi_2^2$
Secondary cellulose acetate	acetone	0.25	109	1.5
		0.5	110	1.0
		0.75	164	1.0
		1.0	167	1.1
	pyridine	0.25	84	1.9
		0.5	110	1.3
		0.75	97	1.1
		1.0	94	1.0
Cellulose triacetate	chloroform	0.25	255	1.95
		0.5	88	1.05
		0.75	50	0.8
		1.0	39	0.7
	methylene chloride	0.25	− 103	0.5
		0.5	− 91	0.3
		0.75	− 80	0.25
		1.0	− 62	0.25
Cellulose nitrate	acetone	0.25	− 259	1.5
		0.5	− 118	1.1
		0.75	− 57	1.0
		1.0	− 32	0.9
	nitrobenzene	0.25	1664	8.0
		0.5	707	4.0
		0.75	400	2.7
		1.0	222	1.95
Ethyl cellulose	n-amyl methyl ketone	0.25	449	3.1
		0.5	457	2.5
		0.75	427	2.2
		1.0	425	2.05
	benzene	0.25	594	3.1
		0.5	631	2.8
		0.75	667	2.8
		1.0	688	2.85

Some typical values are given in Table IV, ϕ_2 being calculated from the density of the dry polymer. Values for the unambiguous secondary acetate and ethyl cellulose systems may probably be regarded as effectively constant. Those for the cellulose nitrate systems (with the exception of that involving nitrobenzene) and the triacetate–methylene chloride and triacetate–tetrachlorethane systems become less negative as the concentration increases, perhaps because of varying degrees of solvation. Values for the cellulose nitrate–nitrobenzene and triacetate–chloroform systems decrease with increasing concentration.

Solvation, the relatively large size of the chain segments, and the limited flexibility of the chains may all contribute to reducing the values of $\Delta\bar{S}_1$ below those obtained for systems involving less polar and more flexible polymers. In the case of the nitrate, more extensive solvation may reduce $\Delta\bar{S}_1$ to near ideal values. The relatively high values for the ethyl cellulose–benzene and ethyl cellulose–carbon tetrachloride systems might be due to the absence of solvation; it has been suggested that the chains are more flexible in benzene than in polar solvents [18]. Simpler lattice theories predict an initial fall in the value of $\Delta\bar{S}_1$ and a subsequent increase as the concentration of polymer increases. The typical values in Table IV suggest that this may be so.

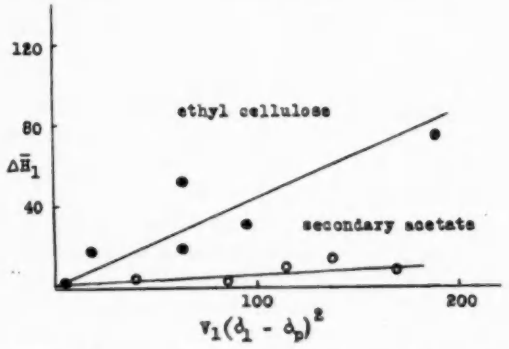

Fig. 6. $\Delta\bar{H}_1$ versus $V_1(\delta_1 - \delta_p)^2$ for ethyl cellulose– and secondary acetate–solvent systems.

According to simpler lattice theories [8, 12], $\Delta\bar{F}_1$ is given by

$$\Delta\bar{F}_1 = RT\left[\ln(1-\phi_2) + (1-1/n)\phi_2 + \chi_1\phi_2^2\right] \quad (9)$$

where n is the number of segments in the polymer chain. Values of the interaction parameter χ_1 can be obtained from the slopes of the π/c against c plots. χ_1 may be regarded as the sum of heat and entropy contributions:

$$\chi_1 = \chi_h + \chi_s \quad (10)$$

χ_h is equal to $\Delta\bar{H}_1/RT\phi_2^2$. Values of χ_1, χ_h, and χ_s at 30° are given in Table V; systems in which association is probable are excluded. The density of the dry polymer was used in the calculation of χ_1. Mean values of $\Delta\bar{H}_1$ or, in cases where $\Delta\bar{H}_1$ varies with concentration, values for 1% solutions were used in calculating χ_h.

The values of χ_s call for some comment. Ac-

TABLE V. Values of χ_1, χ_h, and χ_s

Derivative	Solvent	χ_1	χ_h	χ_s
Secondary cellulose acetate	acetone	0.44	0.27	0.17
	aniline	0.36	1.37	−1.01
	methyl acetate	0.46	0.31	0.15
	dioxan	0.38	0.21	0.17
	pyridine	0.28	0.17	0.11
	nitromethane	0.44	0.50	−0.06
Cellulose triacetate	chloroform	0.27	0.10	0.17
	methylene chloride	0.31	−0.10	0.21
Cellulose nitrate	acetone	0.18	−0.08	0.26
	n-amyl methyl ketone	−0.02	−0.62	0.60
	n-butyl acetate	−0.02	−0.44	0.42
Ethyl cellulose	acetone	0.40	0.40	0.0
	n-amyl methyl ketone	0.35	0.71	−0.36
	n-butyl acetate	0.32	0.43	−0.11
	benzene	0.32	1.05	−0.73
	carbon tetrachloride	0.36	1.64	−1.28

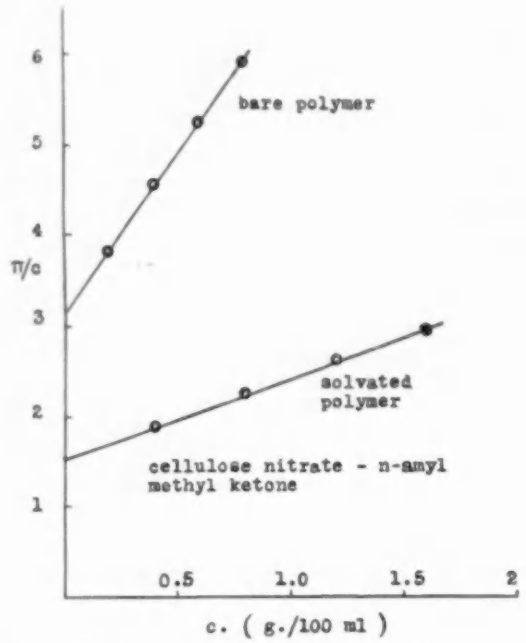

Fig. 7. π/c versus c plots for bare and solvated polymer.

cording to lattice theory, χ_s is the reciprocal of the coordination number. In systems involving flexible polymers its value is found generally to vary between 0.3 and 0.5. Lower values seem likely in systems containing the stiffer chains of cellulose derivatives. Zimm [35] gives $\chi_s = 0.167$ for rods and Baughan et al. [1] a value of 0.12 for cellulose nitrate–solvent systems. With the exception of those involving aniline and nitromethane, values of χ_s for the secondary acetate and triacetate systems are in reasonable agreement with such values. Nitromethane and aniline, however, give negative values which are also obtained with the ethyl cellulose systems, with the exception of that involving acetone with a value of zero. On the other hand, values for the cellulose nitrate systems, with perhaps the exception of acetone, are larger than might be expected.

The zero and negative values of χ_s are associated with large positive heats of dilution and of χ_h. Huggins has given negative values of χ_s for polystyrene–alkyl laurate systems [13]. Boyer and Spencer [3] obtained negative values with polystyrene–divinyl benzene gels. Such systems are more concentrated than those considered here. Huggins [13] suggested that back-coiling in poor solvents might lead to negative values. Back-coiling of relatively stiff cellulose derivative chains seems unlikely and the solvents concerned do not seem to be poor. Association of polymer might possibly lead to similar effects but, with the possible exception of those involving ethyl cellulose in benzene and carbon tetrachloride, there is no evidence for association in those systems with negative values of χ_s. Tompa [34] has pointed out that overlapping of chains may lead to higher values of χ_s than are predicted by simpler lattice theories. The larger values for the cellulose nitrate systems may, however, be a consequence of greater orientation of solvent in solvation [34].

Both Tompa [33] and Munster [23] have considered orientation effects in polar systems. Tompa's treatment involves several empirical constants and, although Munster gives more explicit expressions for $\Delta\bar{F}_1$, $\Delta\bar{H}_1$, and $\Delta\bar{S}_1$, these involve energies or oriented and unoriented configurations. These can be evaluated from values of $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$, but the equations involved are not readily soluble by ordinary means. An alternative and simpler approach to the interpretation of the values of χ_1, χ_h, and χ_s may perhaps be tentatively made. As previously pointed out, solvation is likely to be complete, or nearly so, in the dilute solutions considered. It may be more logical to consider the polymer–solvent interaction as that between solvated polymer and solvent. If the volume fractions of the solvated polymers were known, these could be used to obtain appropriate values of χ_h from heats of dilution. To obtain corresponding values of χ_s, these values of χ_h could be subtracted from values of χ_1 for the solvated polymer–solvent systems, these being obtained from the slopes of π/c against c plots with c expressed in terms of solvated polymer.

Estimates of ϕ_2 and c for the solvated derivatives require knowledge of the numbers of solvent molecules concerned in solvation. For purposes of discussion, certain rather arbitrary assumptions, based on assessments of solvation [22, 27], have been made. It is assumed that one molecule of pyridine, methyl acetate, acetone, and dioxan solvate each unsubstituted hydroxyl group of the secondary acetate, one molecule of nitromethane and aniline solvating each acetyl group. One solvent molecule is assumed to solvate each nitrate group of cellulose nitrate, each acetyl group of the triacetate, and each unsubstituted hydroxyl group of the ethyl cellulose. The weight of solvated polymer will be the com-

TABLE VI

Derivative	Solvent	χ_1	χ_h	χ_s
Secondary cellulose acetate	acetone	0.46	0.20	0.26
	aniline	0.47	0.26	0.21
	methyl acetate	0.47	0.18	0.29
	dioxan	0.43	0.07	0.36
	pyridine	0.37	0.09	0.28
	nitromethane	0.48	0.17	0.31
Cellulose triacetate	chloroform	0.455	0.015	0.44
	methylene chloride	0.45	−0.03	0.48
Cellulose nitrate	acetone	0.43	−0.01	0.44
	n-amyl methyl ketone	0.44	−0.05	0.49
	n-butyl acetate	0.44	−0.05	0.49
Ethyl cellulose	acetone	0.43	0.29	0.14
	n-amyl methyl ketone	0.42	0.38	0.04
	n-butyl acetate	0.40	0.24	0.16

bined weights of polymer and solvating molecules. The density of the solvated polymer may be approximated by dividing this weight by the combined volumes, assuming no volume change in solvation. The concentration of solvated polymer corresponding to a particular concentration of dry or bare polymer can be calculated and the volume fraction of the solvated polymer calculated from its density.

Figure 7 shows a typical plot of π/c against c with c expressed in terms of solvated polymer. A plot with c expressed in the conventional way is included for comparison. Expression in terms of solvated polymer reduces the slope of the plot, increasing the value of χ_1. Values of χ_1 obtained in this way are given in Table VI. Values of χ_h from $\chi_h = \Delta\bar{H}_1/RT\phi_2^2$, using values of $\Delta\bar{H}_1$ for the 1% solutions of dry polymer and with ϕ_2 in terms of solvated polymer, are also given, together with corresponding values of χ_s.

Comparison of these values with those given in Table V shows that consideration in terms of solvated polymer leads to a reduction in χ_h and an increase in χ_s. Values of χ_s for the secondary acetate–aniline and secondary acetate–nitromethane systems are positive and similar to those for the other secondary acetate systems, which are perhaps not unreasonable from the point of view of lattice theories. Values of χ_s for the ethyl cellulose systems are positive; those for the nitrate and triacetate systems are also positive and large, perhaps because of greater orientation of solvent.

It must be emphasized that this approach is tentative and almost certainly oversimplified. The assumptions made regarding solvation are arbitrary and the estimates of the degree of solvation can only be approximate, at best. However, consideration of interaction in terms of that between solvated polymer and solvent may lead to values of χ_h and χ_s in better agreement with simpler lattice theories. It does not, of course, account for the large negative values of χ_s obtained for the ethyl cellulose–benzene and ethyl cellulose–carbon tetrachloride systems. The negative values might be a consequence of association of polymer. It is also possible that polarization of benzene by polar groups of the polymer may occur with subsequent inductive attraction and solvation. Aromatic hydrocarbons may interact with cellulose derivatives in this way [22]. Although carbon tetrachloride is nonpolar, by internal compensation the C–Cl group might have some short-range interaction with polar groups of the polymer.

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Shrinkproofing of Wool with Polyglycine from the Polymerization of Anhydrocarboxyglycine

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Abstract

Shrinkproofing of wool with anhydrocarboxyglycine is not possible from aqueous solution but can be achieved using 2% anhydrocarboxyglycine on the weight of the wool at 50° for 1 hr. in water-washed white spirit or trichloroethylene. Treatments at room temperature require a minimum time of 7 hr. The polymerization, initiated by water present in the wool, produces polyglycine with a degree of polymerization (DP_n) about 30. Descaling of treated fibers shows that all the polyglycine is located in the outside 10% by weight of the fiber; a surface layer can be seen by Sellotape microscopy and electron microscopy. It is this surface layer which is responsible for the large increase in the frictional coefficients μ_1 and μ_2 and decrease in $(\mu_1 - \mu_2)$ which in turn effects shrinkproofing. At levels of treatment $\leqslant 0.39\%$ polyglycine, partial shrinkproofing is produced by small spots of polyglycine distributed at random over the fiber with no appreciable amount of masking of the scale edges.

Introduction

The shrinkproofing of wool with polyglycine produced by the polymerization of anhydrocarboxyglycine (ACG) has been investigated by a number of workers [1, 2, 3, 13], who encountered difficulties due to the instability of the monomer towards moisture. An attempt was made to overcome this difficulty by use of various other N-carboxy acid anhydrides including several sulfur derivatives of greater stability, but no shrinkproofing could be obtained [1]. One of these compounds, thiazolid-

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2:5-dione, has been investigated in this laboratory [9]. It was found that shrinkproofing can be produced from the drycleaning solvent, white spirit (containing 2% n-butanol), at a minimum temperature of 40°. Since there is a considerable amount of evidence that the polymerization of both ACG and thiazolid-2:5-dione is initiated by water on the wool, the use of the more reactive monomer (ACG) should allow satisfactory shrinkproofing to be obtained at room temperature. This is the case providing care is exercised in the purification of ACG and the solvents used. By application of the techniques described in the previous paper [9] it has been possible to establish the location of polyglycine on the wool, its number average degree of polymerization (DP'_n), and the manner in which shrinkproofing is effected.

Experimental

Materials

Anhydrocarboxyglycine. This material was prepared in 60–80% yield by reaction of glycine suspended in dioxane at 50° with phosgene gas according to the second method described by Farthing [12]. The purity of this material, measured by the amount of CO_2 evolved by its polymerization in water in a closed system [5], varied in different experiments from about 70–99%. In those cases where the crude ACG was of low purity it smelled of an acid chloride which effectively prevented shrinkproofing of fabric in ethyl acetate [3], diethyl carbonate [1], or chloroform. Removal of the acid chloride was possible by dissolving the material in a small amount of dimethylformamide, filtering the solution, and precipitating by pouring into chloroform. However, a better method was to dissolve the material in dry ethyl acetate at room temperature, filter off the residue, and precipitate by pouring into excess dry petroleum ether (Shell X222 solvent). In this way the purity of one sample, determined by the CO_2 evolution method, was increased from 83% to 97% and the chloride content, determined by Volhard's method, was decreased from 2.7% to <0.03%. The purified material gave shrinkproofing from chloroform, whereas the crude product or a mixture of the two produced no resistance to felting shrinkage. The purified ACG was used in all the experiments described below.

TABLE I. Shrinkproofing with ACG in Various Organic Solvents*

Solvent	% Solubility of water in solvent at 50°	% Solubility (wt./vol.) of ACG in dry solvent at 50°†	% Area shrinkage (control =40%) after treatment for 20 min.	% Area shrinkage (control =40%) after treatment for 40 min.
Chloroform	0.16	0.03	4	2
Trichloroethylene	about 0.08	0.01	5	2
Petroleum ether‡	about 0.06	<0.001	5	3
Carbon tetrachloride	0.024	<0.001	8	3
White spirit§	about 0.06	<0.001	10	4
Tetrachloroethylene	not known	<0.001	13	3

* Fabric (3.8 g.) treated with 0.1 g. ACG at 50° in 100 ml. water-washed solvent with intermittent stirring.

† Determined gravimetrically. Measurements were difficult to make in water-saturated solvents because of slow polymerization of the ACG.

‡ Boiling range 60–80°.

§ Petroleum fraction, boiling range 150–205°.

Wool. The fabric and Lincoln 36's top used were the same as in a previous paper [9]. All samples were conditioned in the laboratory before use, unless otherwise stated.

Methods

Treatment of wool with ACG. Fabric squares (about 4 g.) were treated with ACG in solution with intermittent stirring which prevented uneven treatment. Lincoln 36's top to be used for shrinkage tests and detailed chemical and physical examination was treated with ACG in trichloroethylene or toluene; the solvent was washed with warm water prior to use to remove inhibitors. Loosely adhering polyglycine and unreacted ACG were removed by washing the wool in acetone or ethyl acetate.

Glycine analyses of whole fiber and cuticle-rich material. About 0.4-mg. samples were analyzed by the dinitrophenylation method [7].

Determination of N-terminal end groups. The dinitrophenylation method was used as previously described [9].

Felting shrinkage, bursting strength, and abrasion resistance. Measurements were made in the usual way [9].

Frictional properties. The coefficients of friction of Lincoln 36's fibers were measured by the capstan

method of Lipson and Howard [15] with a fixed load of 200 mg. on the fiber, except in those few cases where the limitations of the chainomatic device required the use of 100 or 300 mg. The fiber and keratin rod were lubricated with 0.05 *M* borax solution containing 0.02% Teepol.

Microscopy. Snippets of treated and untreated wool were mounted in Sellotape [8, 10, 11] and ≤ 200 were classified into four different groups consisting of (0) untreated, (1) fibers covered with small spots of polyglycine with no evidence of scale masking, (2) fibers covered with a large number of spots but incomplete coverage of the surface, and (3) fiber surface covered completely with polyglycine. The number of fibers in each category was multiplied by the number in parentheses and the three figures summed to give a total figure indicative of the amount of surface coverage by polyglycine [10].

TABLE II. The Effect of Inhibitors in the Solvent on Shrinkproofing with ACG*

Solvent	Treatment of solvent	% Area shrinkage (control = 40%) after treatment for 20 min.	60 min.	120 min.
Chloroform (AR 0.75% ethanol)	Nil	18	1	—
Chloroform (AR 0.75% ethanol)	Water added dropwise to sat. at room temp.	10	—	—
Chloroform (AR 0.75% ethanol)	Water-washed and sat. at room temp.	4	—	—
Chloroform (AR 0.75% ethanol)	Water-washed and sat. at room temp., stored 16 hr. before use	10	—	—
Trichloroethylene (Lab. reagent)	Nil	40	—	25
Trichloroethylene (Lab. reagent)	Water-washed and sat. at room temp.	8	—	—

* Fabric (3.8 g.) treated with 0.1 g. ACG at 50° in 100 ml. solvent with intermittent stirring.

Results

Shrinkproofing Treatments

Effect of solvent. Treatments of fabric with ACG in distilled water at room temperature or at 2° produced no shrinkproofing whatsoever, in agreement with the results of previous workers [3], because the polyglycine does not attach itself to the fabric but precipitates in the solution. The same behavior is observed with thiazolid-2:5-dione [9], but it is to be noted that polyglycine can be grafted to soluble proteins using ACG at 2° [14, 22].

The results of treatments in various organic solvents are given in Table I. The solubility of ACG is considerably increased by using water-saturated rather than dry solvents; e.g., in trichloroethylene there is an increase from 0.01 to 0.04%.

The reasonable correlation between shrinkproofing (Columns 4 and 5) and solubility (Columns 2 and 3) in Table I is probably due to the limitation of the shrinkproofing process by the solubility of the ACG in the water-saturated solvent. Other solvents including toluene, ethyl acetate [3], and diethyl carbonate [1] have been used, but attention was centered on the drycleaning solvents because of the possible development of a practical treatment.

Effect of inhibitors. The polymerization of ACG is inhibited by a wide range of chemicals which cause inhibition by reaction with the initiating species (water, amines, etc.) and/or with the growing end

TABLE III. Glycine Content of Whole Fiber and Cuticle-Rich Material

Sample number and treatment*	Glycine content of whole fiber: Untreated (mole/10^4 g. material at 65% RH and 20°)	Treated (mole/10^4 g. material at 65% RH and 20°)	Increase due to treatment (g./100 g. material)	Glycine content of cuticle-rich material: Untreated (mole/10^4 g. material at 65% RH and 20°)	Treated (mole/10^4 g. material at 65% RH and 20°)	Increase due to treatment (g./100 g. material)	Mean depth of descaling in % of diam.†
1	5.1	6.1	0.8	4.8	15.4	8.0	2.5
2	5.1	7.6	1.9	4.8	32.4	20.7	2.3

* See Table IV for details of treatments.

† Calculated by the fraction (increase in glycine in whole fiber) × 100/(increase in glycine in cuticle-rich material) × 4, which is based on the assumptions that all the polyglycine is located in the layer removed by descaling and that the treated fiber is of approximately uniform density throughout.

of the polymer chain, which is a free amino group [18]. Inhibitors of polymerization of ACG on wool prevent shrinkproofing and may arise from impurities in the ACG (see above), the solvent, and the wool. Impurities in the solvent can be easily removed by washing three times with hot water; this treatment is necessary before any shrinkproofing with ACG is possible in carbon tetrachloride, white spirit, or tetrachloroethylene. With chlorinated solvents these inhibitory substances are produced fairly rapidly; hence the washing must be conducted just prior to use (see Table II). Tests on a knitted fabric showed that it could not be shrinkproofed by treatment with ACG until inhibitory material had been removed by soap and soda scouring or by shaking with several changes of trichloroethylene. The addition of benzoyl chloride inhibited shrinkproofing with ACG to about the same extent as obtained with thiazolid-2:5-dione [9].

Effect of water. The experiments of Baldwin et al. [3] on the shrinkproofing of wool with ACG in ethyl acetate solution were repeated with similar results; no shrinkproofing occurred under anhydrous conditions or using dry ethyl acetate and wool conditioned at 65% RH and 20°, but shrinkproofing was possible on the addition of 2% (vol./vol.) of water. Therefore water is essential for shrinkproofing, and dry ethyl acetate partially dehydrates a conditioned fabric to such an extent that shrinkproofing cannot be achieved [9].

Effect of fabric pretreatment. Fabric squares were immersed in buffer solutions (pH 3–9) for 90 min., washed with running water for 5 min., and then conditioned at 65% RH and 20°. Fabrics pretreated with buffer solutions between pH 6 and 9 were shrinkproofed, but there was no resistance to felting between pH 3 and 5, in agreement with the results of Alexander et al. [1].

Effect of temperature. Most experiments were carried out at 50° when shrinkproofing was obtained in about 20 min. using 2.5% ACG on the weight of the wool (see Table I). Shrinkproofing at 20° was obtained by vigorous shaking in water-washed chloroform for 3 hr. with 2% ACG or in water-washed white spirit for 7 hr. with 2.5% ACG on the weight of the wool (40 hr. with intermittent stirring).

Summary of best practical conditions. The best treatment is probably that in which water-washed white spirit (or trichloroethylene) is used at 50° for 1 hr. with 2% ACG on the weight of the wool and a liquor: wool ratio of about 25:1. This represents a considerable saving in costs of ACG and solvent over those treatments previously advocated [1, 3], but the high cost of ACG precludes its use in practice.

Bursting strength and abrasion resistance of fabrics. Fabrics shrinkproofed by the above treatment (area shrinkage = 1%, control = 40%) showed no change in dry bursting strength and 7% increase in wet bursting strength over the control. In a Martindale abrasion tester the treated fabric gave 40% less weight loss per 1000 rubs and withstood 1.5 times as much rubbing as the control before showing a hole. This result is similar to that obtained using fabric shrinkproofed with thiazolid-2:5-dione [9], but the treated fabric of Baldwin et al. [3] withstood three times as much rubbing as a control.

Glycine Content of Whole Fiber and Cuticle-Rich Material

Two samples of Lincoln 36's top were shrinkproofed with ACG as described in Tables III and IV and glycine analyses performed on whole fiber and cuticle-rich material, obtained in 0.6% yield by the descaling method [6, 7]. The good agreement between the calculated value of 2.4% for the average depth of descaling and the maximum figure of 3% [7] justifies the assumption that all the polyglycine is located in the layer removed by descaling.

N-Terminal Glycine Content of Top and DP_n of Polyglycine

The N-terminal glycine contents obtained from duplicate 12-hr. hydrolyses of five samples of dinitrophenylated wool are recorded in Table IV. In order to correct for the decomposition of DNP-glycine during hydrolysis in HCl, two experiments were carried out in which additional DNP-glycine was added. Values of 35% and 39% were obtained for the percent decomposition of the added DNP-glycine, in good agreement with the value of 37% obtained previously [9]. DP_n was calculated from the results in Table IV by the method described in detail elsewhere [9].

Correlation of Felting Shrinkage of Polyglycine-Treated Top with Frictional Coefficients and Microscopy

Lincoln 36's top was treated with ACG at six different levels (0.21, 0.42, 0.83, 1.67, 3.34, and

6.67% on the weight of wool) in water-washed toluene for 16 hr. at 50°, with liquor : wool ratio of 25 : 1. The felting shrinkage at each level was determined in duplicate together with the degree of coverage of the surface by optical microscopy and the frictional coefficients. The results are summarized in Figures 1 and 2.

Discussion

There is a controversy in the literature as to whether the polymerization of ACG on wool is initiated by the ε-amino groups of lysine [3] or by water [1]. We have found that the polymerization of thiazolid-2 :5-dione is initiated by water [9], and the following evidence is put forward in support of the same thesis for ACG. First, no shrinkproofing of wool with ACG can occur in the absence of water, in agreement with the experimental results of Baldwin et al. [3]. Second, the rate of shrinkproofing is not altered by pretreatment of the fabric with buffers in the range of pH 6–9, although the ε-amino group of lysine would change from the charged form at pH 6 (which does not initiate polymerization [5]) into an equilibrium mixture of the uncharged form (which does initiate polymerization in soluble proteins in aqueous solution [14, 22]) and the charged form at pH 9. Finally, only the initial monolayer of that part of the polyglycine which is deposited on the surface (about 50% in the case of Sample 2 forming a layer about 1000 Å thick [7]) could possibly be initiated by the ε-amino groups of lysine in the wool.

We therefore conclude that water initiates the polymerization of the ACG under our experimental conditions, although it has been found that initiation by ε-amino groups of lysine occurs in aqueous solution (pH 7–9) at 2° with soluble proteins [14, 22]. Since our treatments were carried out in an organic solvent at a much higher temperature and in a heterogeneous system [4], it is reasonable to suppose that a different mode of initiation could occur in the two cases. The polyglycine deposits on the wool without being chemically attached to it but is nevertheless bound quite strongly by intermolecular hydrogen bonds.

The calculation of DP_n in Table IV is based on the assumption that none of the free amino groups at the end of the growing polyglycine chain are removed by a termination reaction. However, this assumption is not valid, as there are two possible

TABLE IV. DP_n of Polyglycine Attached to Wool

Sample number	Treatment	Increase of glycine content on treatment (g./100 g. material)	N-terminal glycine content* (mole/10^4 g.)	DP_n
—	Nil	—	0.013	—
1	2.5% ACG on wt. of wool at 50° for 1 hr. in water-washed trichloroethylene with liquor : wool ratio of 25 : 1	0.8	0.032	32
1A	Sample 1 subsequently immersed in water-washed trichloroethylene for 16 hr. at 50°	0.8	0.026	47
2	6% ACG on wt. of wool at 50° for 17 hr. in water-washed trichloroethylene with liquor : wool ratio of 25 : 1	1.9	0.026	112
3	6% ACG on wt. of wool at 50° for 18 hr. in water-washed toluene with liquor : wool ratio of 25 : 1	2.6	0.038	80

* The average 12-hr. hydrolysis figures for N-terminal alanine, aspartic acid + glutamic acid, serine, threonine, and valine of 0.0054, 0.0060, 0.016, 0.040 and 0.0082 are in reasonable agreement with previous results [9].

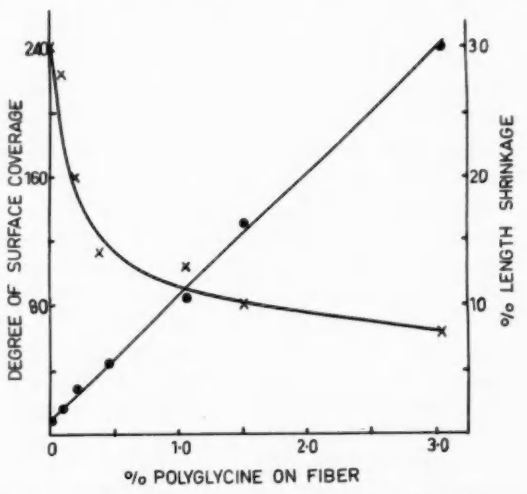

Fig. 1. Effect of percent polyglycine on the fiber on percent length shrinkage (×) and degree of surface coverage as determined by optical microscopy (•).

types of termination reaction. The first, which occurs during polymerization and is favored by increase of temperature, involves the addition of a molecule of ACG in such a way as to produce a substituted urea structure and a terminal carboxyl group [19, 20]. The second is the reaction of free amino groups with impurities in the solvent. This evidently occurred when Sample 1 was subsequently immersed for 16 hr. in trichloroethylene at 50° (see Table IV). However, the decrease in free amino groups observed is not sufficient to account for the large differences between the results of Sample 1 and Samples 2 or 3. It is therefore likely that the first type of termination mechanism is also operative, although it is possible that DP_n actually increases with increasing time of treatment. The values of DP_n listed in Table IV are therefore greater than the correct ones by an indeterminate amount which depends on the amount of the termination reaction. As the latter is likely to be relatively small in 1 hr. at 50°, a value of about 30 for Sample 1 seems reasonable. Other workers have obtained a $DP_n \sim 29$ in the polymerization of ACG in dry ethyl acetate (see [21], Table I). This figure is considerably higher than the value of 18 for polyglycine obtained by the polymerization of thiazolid-2:5-dione on wool.

Unsuccessful attempts have been made to locate the position of the polyglycine on the fiber by dyeing methods [1, 9], but Makinson [16] concluded from microscopy and frictional tests that some of the polyglycine is located on the surface. The first definite evidence obtained in this laboratory was by descaling of fibers containing polyglycine from the polymerization of thiazolid-2:5-dione. The results indicate that about $70 \pm 30\%$ of the polyglycine is located in the outside 12% by weight of the fiber [9]. The results in Table III for ACG polymerization show that all the polyglycine is located in the outside 10% by weight of the fiber. The most conclusive evidence for a layer of polyglycine actually on the surface of the fiber is that the polymer can be seen by optical and electron microscopy [10]. It is found that for a particular weight of polyglycine on the fiber there is an equal amount of polyglycine on the surface in both the thiazolid-2:5-dione and ACG treatments [10].

Mechanical and swelling forces produce movement of parts of wool fibers in such a way that they cannot return to their original positions [8]. This net movement of fibers in the direction of their root ends

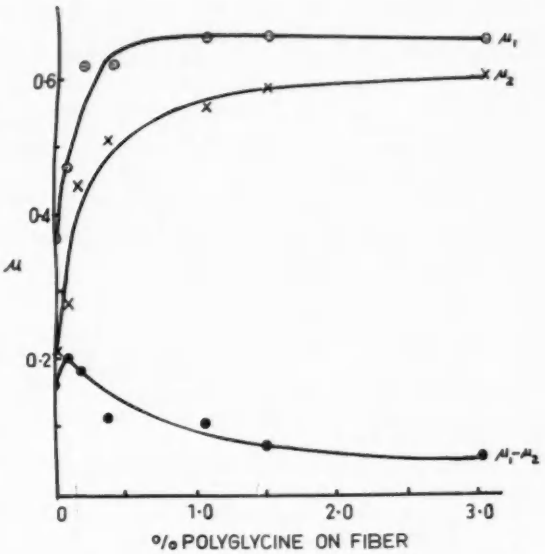

Fig. 2. Effect of percent polyglycine on the fiber on the antiscale coefficient μ_1 (⊙), the with-scale coefficient μ_2 (×), and $\mu_1 - \mu_2$ (●).

[17] is accompanied by fiber entanglement and felting. The rootward migration can be prevented and hence shrinkproofing effected by increase of μ_1 and μ_2 and by decrease of $(\mu_1 - \mu_2)$. Thus the large increase in μ_1 and μ_2 shown in Figure 2 is a primary cause of shrinkproofing (particularly at levels of treatment less than 0.6% polyglycine), and the reduction in $(\mu_1 - \mu_2)$ is also a contributing factor which becomes increasingly important at higher levels of treatment. The lack of any evidence for spot-welding of fibers in this case shows that this effect does not contribute to shrinkproofing; see [9] for detailed discussion.

It is clear from Figures 1 and 2 that the frictional changes which effect shrinkproofing are a direct result of the deposition of polyglycine on the surface of the fiber. Microscopic examination of fibers at levels of treatment $\leqslant 0.39\%$ polyglycine shows that all fibers fall into Class 0 or 1 [10]. The large increase of μ_1 and μ_2 and the reduction of the felting shrinkage to 14% (control = 30%) is therefore brought about without appreciable alteration of the asperities of the scales, which are still clearly visible. It is only at levels of treatment above about 1% that an appreciable numbers of fibers are found in Class 2 or 3; i.e., appreciable masking of scale edges

occurs with further increase of μ_1 and μ_2, decrease of $(\mu_1 - \mu_2)$, and decrease of felting shrinkage.

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Mass Transfer and the Washing Process

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Abstract

Published soil removal data suggest that the mass transfer process in a washing machine (transport of materials between cloth and bath) may influence or even dominate the soil removal process. Therefore, mass transfer is investigated in a small scale washer (Terg-O-Tometer).

The process is characterized by the transfer coefficient, which is the inverse of the time constant. It is correlated using dimensional analysis with such variables as the bath volume, the water-holding capacity of the cloth load, the agitation speed, and stroke angle.

Actual experiments are conducted with water-soluble substances; their results support the theoretical developments set forward. The transfer coefficient is directly proportional to agitation speed and stroke angle, inversely proportional to the water-holding capacity of the cloth load, and independent of the bath volume.

Finally the mass transfer process is compared in a full-size machine, a small commercial washer, and the test device by scale-up experiment. Good agreement is found, thus confirming the full-scale application of the results.

Introduction

The complexities involved when a piece of soiled fabric is subjected to the laundry process have been and for the most part still are quite foreboding. Even though the process, in general, is enormously complex, many investigators have made one or more forays at its various facets [1, 4, 5, 7, 10, 11]. After a general study of the literature available on the washing process it was felt that some small insight had been gained which led to the hypothesis set forward here.

The soil removal during washing can best be shown by a curve representing the percentage of soil removed as a function of time. In most cases the curve resembles an exponential decay function approaching asymptotically with elapsed time a steady percentage of soil removal. This steady percentage, however, will always be less than 100%. Good correlation has been obtained between experimental curves and the theoretical relationships set forth by Vaughn [12] and Utermohlen [11]. Similar curves are obtained in simple mass transfer processes [9]. Therefore, the hypothesis that mass transfer may play a dominant role in the washing process seems very likely.

Mass transfer in the washing process is understood to be the process by which fresh detergent is conveyed from the bath to the cloth surface and by which the soil materials are transported away into the detergent bath. We are tempted to believe that the detachment of the soil from the fiber surfaces takes place mainly by chemical action, at least in the case of small soil particles. Consequently, the main influence of mechanical action would be reserved for the mass transfer process. Such a view is supported by experiments in colloid chemistry on the peptization of flocculated particles. Generally, colloids of particles below 1 μ are impossible to peptize by mechanical action alone. This would indicate that the cohesion forces between particles are much larger than the forces which can be imparted by fluid shear [6]. It is felt that these same forces are responsible for the retention of soil particles on a cloth surface.

When molecularly divided matter is transported, mass transfer is synonymous with diffusion. As defined here, mass transfer also includes the transport of colloidal, liquid, or solid macroscopic materials. In all cases the transfer rate, independent of the materials involved, is proportional to the concentration gradient present in the dispersing medium. When the material to be diffused is initially concentrated on a solid surface and is subsequently diffused in a liquid medium, it is usually assumed that the concentration gradient is restricted to a film in the neighborhood of the solid surface. Under this assumption the concentration of the remaining portion of the liquid medium may

be considered essentially uniform. This assumption is particularly applicable when the process occurs under conditions of strong agitation.

On the basis of the above hypothesis, which holds at least for some soil types, the mass transfer process for a conventional agitator washer was investigated under various conditions. Whereas no identity is claimed between mass transfer and actual soil removal, important conclusions could be expected from a study of mass transfer. Furthermore, the ease and precision of the methods used here are much superior to those obtainable in actual soil removal tests.

Theory

Considering the transfer of some material from the cloth load to the liquid bath, which is originally clean, the instantaneous concentration in the bath is given by the equation (see Appendix for detailed development and Table I for definition of symbols):

$$C_s = -(C_\infty - C_{so}) \exp\left[-KA\left(\frac{1}{V_c}+\frac{1}{V_s}\right)t\right] + C_\infty \quad (1)$$

TABLE I. Definition of Symbols

A	Interfacial transfer area	cm.²
B	Diffusion coefficient	cm.²/sec.
B_0	Self-diffusion coefficient of water	cm.²/sec.
C_c	Theoretical concentration of material on the swatch	g./cm.³
C_{co}	Initial concentration of the contaminant solution	g./cm.³
C_s	Theoretical concentration of the bath	g./cm.³
C_{so}	Initial concentration of the bath	g./cm.³
C_∞	Equilibrium concentration after infinite time period	g./cm.³
D	Diameter of the test device	cm.
d	Macroscopic particle diameter	cm.
d_0	Water molecule diameter	cm.
g	Gravitational constant (981 cm./sec.²)	cm./sec.²
K	Mass transfer constant	cm./sec.
M	Dimensionless numerical constant	
N	Agitator speed	rev./sec.
N_r	Reynolds number	
S	Numerical exponent	
t	Time	sec.
V_c	Volume water content of the cloth load	cm.³
V_s	Volume of liquid bath	cm.³
w	Transfer coefficient	1/sec.
x	Numerical exponent	

Greek letters

α	Stroke angle	radians
ν	Kinematic viscosity	cm.²/sec.
ρ	Mass density	g./sec.²
σ	Surface tension	g./cm.
ω	Angular velocity	radians/sec.

as a means of simplification we will let

$$w = KA\left(\frac{1}{V_c}+\frac{1}{V_s}\right) \quad (2)$$

in which w is the inverse of a time constant. By transforming Equation 2, our transfer constant, K, becomes

$$K = \frac{w}{A}\left(\frac{V_s V_c}{V_c + V_s}\right) \quad (3)$$

If the value of V_c is assumed to be very much smaller than V_s, our value for K becomes

$$K = \frac{wV_c}{A} \quad (4)$$

When the transfer conditions are as described earlier and the initial concentration of the liquid medium is zero (i.e., $C_{so} = 0$) Equation 1 takes the form

$$\left(1 - \frac{C_s}{C_\infty}\right) = e^{-wt} \quad (5)$$

A plot of Equation 5 on semilog paper will result in a straight line. The slope of this straight line will be our value w. The relationship designated by Equation 5 is valid even for the mixing of dry granular materials [2]. The coefficient w determines the time rate of the mass transfer process. As may be seen from inspection of Equation 2, this coefficient incorporates such variables as A, the interface area across which the mass transfer takes place; V_s, the volume of the liquid bath, and V_c, the volume of liquid initially containing the transfer material (i.e., the water content of the cloth). The mass transfer constant, K, will depend on the type of transfer materials involved, the geometry of the device, and the mechanical agitation involved (both the type and manner of application). There is a vast amount of literature concerning the dependence of K on these variables. A summary of this literature can be found in the thesis of Ryan [9].

In order to generalize the validity of any data obtained from a particular test device it is convenient to combine the variables into dimensionless groups. Such a procedure is outlined in a paper by Ruston [8]. According to this approach, mass transfer data would then be correlated by the following equation:

$$\left(\frac{KD}{B}\right)\left(\frac{\nu}{B}\right)^{-s} = M\left(\frac{D^2\omega}{\nu}\right)^x \quad (6)$$

The dimensionless groups involved are

$$\frac{KD}{B} = \text{Mass transfer number}$$

$$\frac{\nu}{B} = \text{Schmidt number}$$

$$\frac{D^2\omega}{\nu} = \text{Reynolds number}$$

and the exponents x and s must be determined by experiment. Furthermore, if the effects of gravity and surface tension become important, these additional groups would have to be included:

$$\frac{D\omega^2}{g} = \text{Froude number}$$

$$\frac{\rho\omega^2 D^3}{\sigma} = \text{Weber number}$$

Similarly, in the case of a reciprocating rotational agitation, the angle of stroke (a dimensionless quantity) may be another independent factor to be included.

In Equation 6, besides the experimentally determined coefficient, K, only the viscosity, ν, and the diffusion constant, B, will depend on the temperature and the materials involved. Consequently, the dependence of K on the Reynolds number, N_r, should not be affected by a change of the materials involved in the mass transfer process. For this reason, mass transfer was investigated using water-soluble substances. The diffusion coefficient of dissolved substances in water is remarkably uniform and of the order of magnitude of 10^{-5} cm.^{2}/sec. [3]. The diffusion coefficient of microscopic particulate matter or colloidal particles in water is expressed by

$$B = \frac{d_0 B_0}{d} \tag{7}$$

Therefore, once the unknown exponents and the coefficient K are determined experimentally, the transfer process of any material other than the test material can be predicted.

To determine the relationship between different size washers, the dimensional analysis technique yields (from Equation 6 with ν and B considered constants)

$$KD \propto (D^2\omega)^x \tag{8}$$

Now the relationship between the transfer constant, K, and the transfer coefficient, w, is (see Equation 4)

$$w = \frac{KA}{V_c} \tag{9}$$

However, A, the fictitious interface area, and V_c, in our case the water-holding capacity of the cloth, are of a geometric nature and should vary according to the scale proportions. Therefore, the above relation leads to the proportionality

$$wD \propto K \tag{10}$$

By substitution of Equation 10 into Equation 8

$$w \propto \omega^x D^{2x-2} \tag{11}$$

As it will be shown, experimental results led to a value of x equal to one (see Equation 17); consequently Equation 11 becomes

$$w \propto \omega \tag{12}$$

This expression, Equation 12, predicts that the transfer coefficient, w, should not vary when the size of the apparatus is changed. This prediction will hold true provided the devices to be compared are geometrically similar and all the other variables, such as agitation speed, material to be diffused, the fluid medium, and the temperature remain the same.

The form for the Reynolds number used in this work is as follows:

$$N_r = \frac{\omega D^2}{\nu} \tag{13}$$

However, the angular velocity of the agitator may be written

$$\omega = 2\alpha N \tag{14}$$

By substitution of this result in Equation 13, our generalized Reynolds number should be written

$$N_r = \frac{2\alpha N D^2}{\nu} \tag{15}$$

This form for the Reynolds number is used to take into account not only variation in the speed, N, but also to account for variation in the size of the stroke angle, α.

Experimental Technique

It was decided to study the mass transfer process through the use of a Terg-O-Tometer type test unit (Figure 1). This device consists of a cylindrical plastic container (diameter $3\frac{3}{4}$ in., depth $6\frac{3}{4}$ in.) and a vertically-positioned oscillating agitator. The number of strokes, stroke angle, temperature, and pressure can be controlled in the device. The test unit can be considered a small scale model of an agitator-type washing machine,

with slight differences in geometry. For the actual test procedure, five swatches (3 × 5 in. AHLMA test material) were soaked for 5 min. in a 3% by weight cupric sulfate solution. The plastic container was filled with 275 ml. of deionized water and the agitator set in motion. The cloth swatches were then introduced into the container and the ensuing diffusion of material from the cloth into the bath was recorded. It was possible to record the diffusion process by continuously measuring the electrical conductivity of the bath and feeding the signal to an appropriate recording instrument. (Note conductivity probe in the wall of the plastic cylinder.) The recording instrument had previously been calibrated on solutions of known concentration. The recorded curves were plotted on semi-log paper according to the previously described theoretical analysis. The slope of the resulting straigh line, w, was then determined.

Fig. 1. Terg-O-Tometer type test unit. The face of the conductivity probe is shown in the wall of the test cylinder.

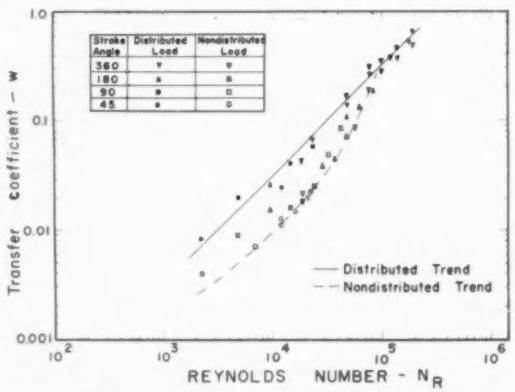

Fig. 2. Transfer coefficient, w, versus the Reynolds number. The agitator speed ranged between 10 and 90 strokes per minute.

As a final step in this phase of the mass transfer study, three different size washing devices were compared experimentally. The largest was a full-size automatic washer with a 21-in. tub diameter. This washer has a fixed stroke angle of 180° but may be operated at a speed of either 48 or 72 strokes/min. An intermediate size washer with a $13\frac{3}{4}$-in. diameter tub was also available. The stroke angle on this washer was also 180° but only one speed (68 strokes/min.) could be used. Of course, the third size washer was our Terg-O-Tometer type test device. It was operated at speeds of 48 and 70 strokes/min. with the stroke angle fixed at 180°.

A strict geometric similarity would require not only the same proportion between the measurements of the different size washers but also a scale-up of the cloth structure. Whereas the first requirement is sufficiently fulfilled by the three devices, the second was impossible to satisfy. The same type of cloth (AHLMA towel) was used but the amount of cloth chosen was such that its water-holding capacity satisfied the proportions prescribed by similarity. The cloth was first soaked in a detergent (All) solution of high concentration. Then it was rinsed in tap water (at approximately 100° F.). The rinsing curve was recorded by measuring the conductivity of the bath solution. These recordings have been transferred to a semilogarithmic plot.

Results and Discussion

In Figure 2 the transfer coefficient, w, is plotted against the Reynolds number. The Reynolds number takes into account variations in speed and stroke angle. The effect of distributed vs. non-distributed load conditions may be noted. At high Reynolds numbers, this effect is not evident because a load introduced in a non-distributed condition is quickly redistributed by the action of the agitator. However, the transfer coefficient falls off sharply when a load remains in a non-distributed condition.

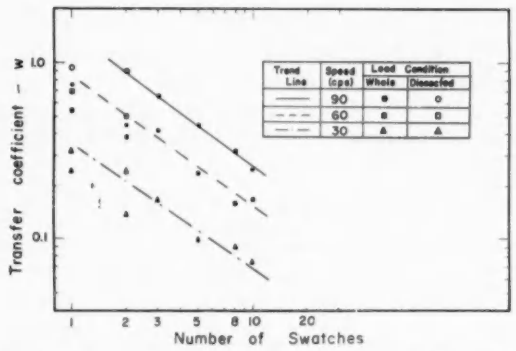

Fig. 3. Effect of cloth loading on the transfer coefficient. A constant stroke angle of 180° was maintained for all speeds.

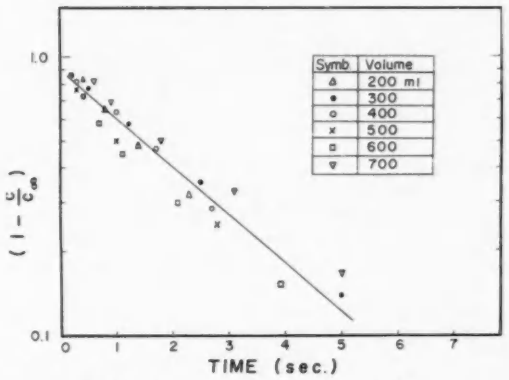

Fig. 4. Effect of bath water level on the rate of mass transfer. Agitator speed was held constant at 92 strokes/min. with a fixed stroke angle of 360°.

In the relationship between w and ω, the angular velocity, observe that Equation 6 may be written

$$\left(\frac{wD^2}{B}\right)\left(\frac{\nu}{B}\right)^{-s} = M\left(\frac{D^2\omega}{\nu}\right)^{x} \tag{16}$$

If all the variables are maintained constant, except w and N, this equation reduces to the proportionality

$$w \propto \omega^x \propto N_r^x \tag{17}$$

From the direct proportionality, obtained experimentally between w and N_r, the value of the exponent x is found to be one. Therefore, the transfer coefficient, w, is directly proportional to the speed of the agitator and to the stroke angle.

In order to test the effect of the amount of loading on the transfer coefficient, runs were made employing various quantities of cloth (number of swatches). These data are shown in Figure 3. It is interesting to note on this figure the effect of load distribution. For three or more swatches a clean trend relating the transfer coefficient w and the number of swatches may be noted. However, for loads of one or two swatches the trend apparently does not hold. It is felt that this is the result of poor load distribution. To test the validity of our distribution theory a single swatch (3 × 5 in.) was cut into four symmetrical portions. The transfer curve was then re-run with this dissected swatch and the transfer coefficient determined. This dissection procedure was repeated for a two-swatch load. The results of these dissected swatch runs are shown in Figure 3 and seem to confirm our prediction of distribution effects. Once this correlation for distribution effect is made, an inverse relationship is found between the transfer coefficient and the number of swatches.

The inverse relationship can be explained by the following theoretical consideration. Provided the volume of the bath, V_s, is much larger than the volume diffused, V_c, the theoretical relationship

$$w = K.1\left(\frac{1}{V_c} + \frac{1}{V_s}\right) \tag{18}$$

can be modified to

$$w = \frac{AK}{V_c} \tag{19}$$

The proportionality between w and A, the interfacial area, has been stated in the literature. In the corresponding experiments, however, the interface area was well defined. Unfortunately, in our case the interface area is not well defined. Therefore, the inverse relationship between w and the number of swatches is rather attributed to the variation of V_c, the volume to be diffused (i.e., the water content of the cloth load).

The effect of water bath quantity was also investigated. A sample result is shown in Figure 4. Numerous attempts were made to find a correlation between the transfer coefficient, w, and the water bath volume. In all attempts no clear trend was evident. From the sample data of Figure 4, a certain scatter is evident in the test results. There is apparently, however, no pattern relating this scatter and the water level. This justified the earlier assumption that the effect of the bath volume does not appear in Equation 19.

In order that the results obtained by model experiments will be valid in full-scale applications, it is necessary to test the relationships existing

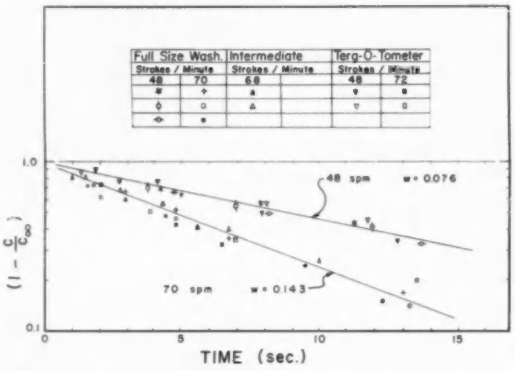

Fig. 5. Mass transfer in similar devices of different size.

between the experimental equipment and the full-scale device (i.e., a washing machine). The dimensional analysis shown in Equation 12 was used to predict the theoretical performance of full-sized washers.

When it is assumed that the material to be diffused and the fluid medium remain the same, identical experiments conducted in three different size washers give a good correlation (see Figure 5). Slight differences among repeated experiments can be justified by the variation of the initial solution content of the cloth. Unfortunately, this solution content could not be precisely controlled.

A slight deviation from the predicted straight-line relationship will be detected for most runs. The cause of the deviation is believed to be the fact that detergent is not a pure substance. It is composed of different compounds which have different diffusion coefficients. As a consequence the recording is a superposition of the transfer process of diverse materials. The elements of highest mobility dominate at the start, whereas only the slowly diffusing elements remain at the end. Since the diffusion constants of water-soluble substances do not differ by more than a factor of ten, only small deviations should result. A much stronger effect should be expected when microscopic solid particles or colloids are involved. The diffusion constant of these materials is a function of particle size and may differ by a factor of as much as 1,000. This may explain why the transfer coefficients as obtained by Vaughn [12] in an actual washing process are much smaller than those encountered here. It also may account for the fact that in general washing curves seldom can be correlated by a straight line on a semilogarithmic plot.

Conclusions

The results of this investigation may be summarized under the following points.

1. The time dependence of the bath concentration in the mass transfer process considered here can be well approximated, at least for pure substances, by a straight line, provided $\left(1 - \frac{C_s}{C_\infty}\right)$ is plotted against time on a semilog plot. The slope of the line, w, is then the transfer coefficient.

2. The relationship between the transfer coefficient and the essential variables can be expressed in dimensionless form.

3. The relation between transfer coefficient, w, and Reynolds number, N_r, is extremely dependent on the condition of the load as it is introduced into the test apparatus. When the load is introduced in a distributed condition the relation between w and N_r is a direct proportionality. However, wide deviation from this proportionality is evident when the load is introduced in a non-distributed manner.

4. The transfer coefficient, w, is the same for similar washers of different size operated under identical conditions.

5. No clear indication of water level effect on the mass transfer process can be determined, since the available data show little or no effect whatsoever.

6. An inverse relationship exists between the transfer coefficient, w, and the amount of cloth loading.

Whereas it is unknown to what extent mass transfer influences soil removal, there is little doubt in our minds that such an influence is present. As can be observed, the effect of several variables is explained by investigating the mass transfer process alone. If actual washing tests should show a deviation from the relationships outlined here, such deviations will be due to the particular nature of the soil and detergent types involved. Keeping in mind these developments, past and future soil removal data will reflect a new interpretation.

Appendix

Since in a mass transfer process the time rate of change of a concentration must be proportional to the concentration difference, the following equations may be written for a system consisting of a cloth load and a liquid bath:

$$V_c \frac{dC_c}{dt} = AK(C_s - C_c) \qquad (1A)$$

and

$$V_s \frac{dC_s}{dt} = AK(C_c - C_s) \qquad (2A)$$

Solving Equation 2A in terms of C_s and integrating, we obtain

$$\frac{C_x - C_s}{C_x - C_{so}} = \exp\left[- KA \left(\frac{1}{V_c} + \frac{1}{V_s} \right) t \right] \qquad (3A)$$

where

$$C_x = \frac{C_c V_c + C_s V_s}{V_c + V_s} \qquad (4A)$$

Equation 3A is the instantaneous concentration of transferred material in the liquid bath.

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Power Consumption of a Terg-O-Tometer

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Abstract

One of the most convenient means of running small-scale tests on washing or rinsing equipment is through the use of a commercially available test fixture called a Terg-O-Tometer. Unfortunately, however, this test fixture does not provide for measurement of the net power transmitted to the liquid bath. Since information on power input is vital to the proper evaluation of a cleaning process, a means was devised to directly measure this power input.

The power input, characterized by the power number, was obtained for various Reynolds number values, where the Reynolds number was used as a measure of the speed and stroke angle variations. Information on power input versus water level variation and varying cloth load quantities was also obtained. In general, net power input increases with increasing water bath volume and increasing cloth-to-water ratio.

Introduction

An intense effort has been made in the past to establish a testing method for the laundry process [1, 6, 7]. In all of these efforts it was felt that the conditions of actual laundering could be approximated. One of the most convenient means of running small-scale tests on washing or rinsing equipment is through the use of a commercially available test fixture called a Terg-O-Tometer.[1] Mechanical action in a Terg-O-Tometer resembles that found in the commercial agitator washer. The Terg-O-Tometer does not provide for measurement of the net power transmitted to the liquid bath. This is somewhat of a handicap since it was soon recognized that the amount of mechanical energy supplied to the device has a strong but unexplored influence on the test results [1, 2, 8]. Because of the usefulness of power consumption data, a means was devised in this investigation to obtain this information by direct

[1] U. S. Testing Co., Hoboken, N. J.

TABLE I. Definition of Terms

D	test device diameter	cm.
g	gravitational constant	cm./sec.^{2}
K	power number	
N	agitator speed	cycles/sec.
N_r	Reynolds number	
P	power	erg/sec.
T	torque	dyne-cm.
Greek letters		
α	stroke angle	radians
ν	kinematic viscosity	cm.^{2}/sec.
ρ	mass density	g./cm.^{3}

measurement. It is hoped that this measuring technique and the results obtained from its successful application will prove of value to persons using this type of test equipment.

Although literature exists on the power consumption of mixing devices with various agitators [3, 5], information on reversing types of motion seems to be lacking. In this investigation the agitator motion consisted of a uniform rotation over a given angle (here identified as the stroke angle) followed by a sudden reversal and uniform rotation in the opposite direction over the same angle. It can be identified with a uniform rotation in a unique sense provided the extra power supplied during the reversal period is very small compared with the power input during the total cycle.

The power consumption of an agitator device can be correlated by a dimensionless expression. As given by Rushton [5] this expression is

$$\frac{Pg}{\rho(2\alpha N)^3 D^5} = K \qquad (1)$$

where the power, P, is given by

$$P = 2\alpha NT \qquad (2)$$

and other terms are defined in Table I. The value of the dimensionless number K, the power number, varies slowly with the Reynolds number. In this investigation the Reynolds number was defined as

$$N_r = \frac{2\alpha ND^2}{\nu} \qquad (3)$$

Typical curves correlating the power number–Reynolds number relationship are given in Rushton's paper [5]. The expressions above were used to determine and correlate the power consumption of a Terg-O-Tometer under various operating conditions. In Rushton's notation D is the effective diameter of the agitator. Since in our case there may be some doubt as to the effective diameter of the agitator and as the ratio between agitator diameter and diameter of the Terg-O-Tometer does not vary, we prefer to identify D with the latter.

Instrumentation

In order to make an acceptable piece of test equipment (see Figure 4), a Terg-O-Tometer cylinder and agitator (Figure 1a) were obtained. The agitator head was removed from the shaft and a new shaft assembly was substituted (Figure 1b). As may be seen in Figure 1b, the new shaft is actually made in two sections and then assembled by the use of a thin-walled aluminum sleeve. Each end of this sleeve has been split and, as the stainless steel nuts are advanced, the sleeve is secured to the two shaft sections by a steady, even application of pressure. Under this assembly, any torque transmitted from the drive shaft to the agitator head must pass through

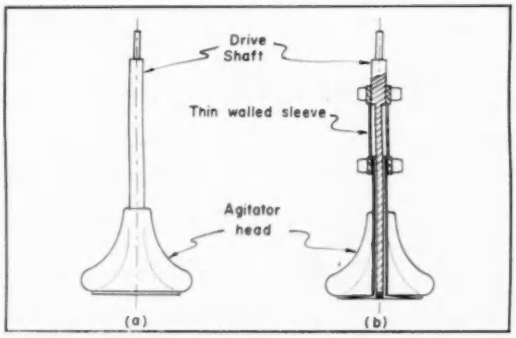

Fig. 1. Comparison of the original agitator (a) and the modified agitator (b) showing the thin-walled sleeve in position.

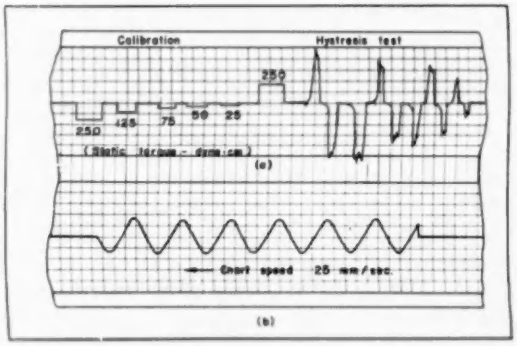

Fig. 2. Reproduction of two-channel Sanborn recording tape showing calibration and hysteresis tests (a) and wave formation and frequency pattern (b).

the "torsion sleeve" connection. This design eliminates the influence of the bearing friction on the torque measurements. This torsion sleeve contains a strain gauge bridge. The type of bridge incorporated was such that the effects of temperature and axial bending strains were eliminated. For a complete discussion of the strain gauge bridge employed, the text of Perry and Lissner [4] is recommended.

In this particular application, SR-4 strain gauges (type A-18, produced by the Baldwin-Lima-Hamilton Corp.) were employed. Duco Cement was used to bond the gauges to the aluminum sleeve. After the cement had thoroughly dried (approx. 48 hr. at room temperature) the entire strain gauge system was covered with a wax coating as a waterproofing precaution.

The strain gauge bridge is calibrated (Figure 2) by the application of static torques to the agitator head. After calibration, the bridge will measure directly the net torque transmitted to the liquid bath. In addition, the linearity of instrument response and the possible hysteresis effects were also checked (Figure 2).

The agitator was driven by a reversing, variable-speed air motor. To measure the instantaneous position of the agitator, a linear wire-wound potentiometer was connected to the air motor shaft. The resistance of the potentiometer was thus a linear function of the angular position of the agitator. Figure 3 shows the assembled test device. (Note the potentiometer mounted on top of the driving motor.)

Fig. 3. Assembled test device. Swatches are shown in the cylinder during an actual test run.

These two signals, one the signal from the strain gauge, indicating torque, and the other from the potentiometer, indicating the angular position of the agitator, were recorded simultaneously on a Sanborn recorder.

The slope of the position-indicator recording is proportional to the agitator speed. This recording shows that the shaft rotates with uniform speed during the first half of a cycle, reverses the direction of rotation almost instantaneously, and rotates in the opposite direction with uniform speed during the second half of the cycle. The torque recording shows a steady torque during the periods of uniform agitator rotation. Unfortunately, the signal is covered by a high-frequency perturbation, due, we believe, to the effect of a chain drive mechanism. As one would expect, the instantaneous reversal of the rotation direction produces a high inertial torque loading. This loading, however, is of quite short duration. In evaluating the mean torque during one cycle, these high inertial peaks have been omitted from consideration. From the point of view of power consumption, the contribution of these peaks is believed to be negligible. Their influence may be important if the time period during which this transient fluid motion dies out is equal to or greater than the duration of one cycle. Such effects may have to be taken into account for this type of motion at very high speeds.

Test Methods and Results

Power Number

The agitation speed of our test device can be varied by a factor of ten at most; consequently the range of Reynolds numbers which can be investigated by varying the speed alone is rather limited. Because of this, the general trend of the power-versus-speed relationship was somewhat uncertain. In order to investigate a greater range of Reynolds numbers, the viscosity of the liquid was increased. This will have the same effect as a decrease in the agitator speed. The power consumption of the test device was determined experimentally for different

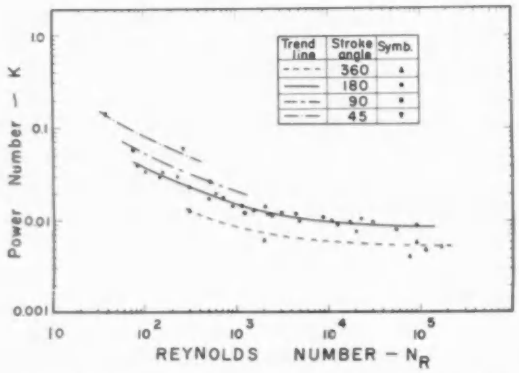

Fig. 4. Power number versus Reynolds number. Speed range on these tests was 50–90 strokes/min. Trend lines are used to indicate the general performance for each stroke angle.

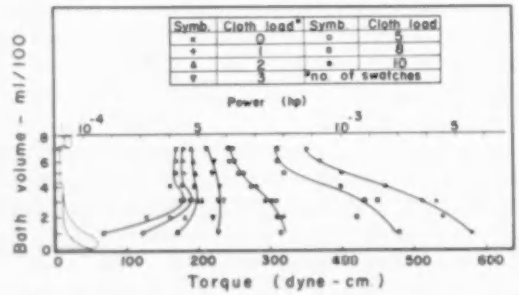

Fig. 5. Water level of the liquid versus power input to the bath. Cloth loading is used as a parameter. Stroke angle 360° and speed constant at 90 strokes/min.

values of agitation speed, stroke angle, and liquid viscosity. In these experiments the contribution of the changes in liquid density has been incorporated into the expression for Reynolds number and power number. Liquids of different viscosity were prepared by mixing glycerin and deionized water in various proportions. For these tests a liquid volume of 275 ml. was selected and no cloth load was employed. The experimental power numbers have been plotted in Figure 4 against the Reynolds number. Although the correlation is satisfactory and agrees with the trends indicated by the data of Rushton, a definite effect of the stroke angle can be observed. Indeed, for the same Reynolds number, the power number increases with decreasing stroke angle.

Water Level Variation

The torque on the agitator shaft was measured for various amounts of water in the test device (Figure 5). In the absence of a cloth load, the torque requirement increases with increasing water level up to a point where the most effective portion of the agitator blades is covered. A further increase in the water level results in a decrease of the torque. In fact, the torque approaches a constant value for high amounts of water. The peaking of the torque value coincides with a very vigorous surface agitation, which may very well be its cause. For high water levels, when the agitator head is far below the water surface, no appreciable surface agitation can be observed.

Loading Effects

As a second parameter in the power consumption measurements, various numbers of cloth swatches were placed in the liquid bath. The presence of this cloth loading has a double effect. It tends to damp out the surface agitation; also, an increasing cloth-to-water volume ratio definitely increases the power input requirements.

A graphical summary of the water level and cloth loading effect is given in Figure 5. As a ready reference, the outline of the actual agitator is shown on the left of this figure. The power required for any combination (within the test limits) of water volume and cloth loading is readily available.

Conclusions

The results of this investigation can be summarized as follows.

1. The relationship between the power number and the Reynolds number, determined experimentally for a reversing type of agitation, follows the general trend observed by Rushton. In order to obtain exact correlation, however, the stroke angle must be introduced in addition to the Reynolds number.

2. Increasing water level results in increased power consumption until the major portion of the agitator head is completely submerged.

3. When a cloth load is introduced into the test device, the power consumption increases with increasing cloth-to-water ratio.

The data obtained from this investigation will provide information on the net power consumption of a Terg-O-Tometer and test devices of a similar nature.

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A Structural Comparison of Films Regenerated from Cellulose Acetate and Viscose[1]

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Abstract

Cellulose films having radically different physical properties were prepared by the standard viscose process and by the deacetylation of commercial cellulose acetate film. These films were characterized by x-ray, acid hydrolysis, differential swelling in caustic, and light and electron microscopy of freshly torn edges.

Measurements by x-ray and acid hydrolysis reveal that the film from cellulose acetate has less crystalline material and smaller crystallite size than the viscose film. By differential swelling in caustic the film from cellulose acetate was shown to have less highly ordered material than the viscose film.

Light and electron microscopy of freshly torn edges of the two films reveal a common structural element. Fibrils were seen, the size of which did not vary appreciably between the two films. The arrangement of the fibrils in the internal structure of the films was markedly different.

By considering the data obtained from these different sources, an explanation of the property difference and its relation to fine structure can be postulated.

Introduction

The structure of polymeric materials can be considered to be the connecting link between the process by which the materials are formed and their physical or mechanical properties. If significant differences are observed between the properties of two samples of a material, corresponding structural differences may be anticipated, provided the methods for defining these structural differences are adequately sensitive. The application of this structure–property relationship is amply illustrated by the excellent work which has been done in developing rayon filaments of ever-increasing tensile and fatigue properties. In the case of films, the desired optimum in structure and properties is more obscure than in fibers. This obscurity is partly the consequence of the very complex system of forces to which films may be exposed under conditions of use. It appears desirable, however, to incorporate into a film toughness or the capacity to absorb work rather than high tensile strength alone. For this study of structure–property relationships, two cellulose films having marked differences in physical properties were used. One was a film produced from commercial viscose in the laboratory and containing no plasticizer. The other was cellulose obtained by the saponification of commercial cellulose acetate film. These films were charac-

[1] Presented at the 137th National American Chemical Society Meeting, Division of Cellulose Chemistry, Cleveland, Ohio, April 6, 1960.

terized by known methods of structural characterization such as x-ray, caustic swelling, etc., and a study was made of how physical failure occurred in these two films. The physical properties of these two films are given in Table I.

It is clear from the above data that the film made by saponifying cellulose acetate is markedly tougher than viscose film in tear strength, impact strength, and elongation. A substantial difference in the structure of these films is therefore expected.

Experimental and Discussion

The viscose films used in this study were prepared from commercial viscose used for the manufacture of cellophane. This viscose was metered onto a glass plate by means of a carefully machined doctoring roll which allowed enough viscose to be deposited onto the plate to make a film 1 mil thick when dry. Coagulation and regeneration were carried out in a regenerating bath containing 12% sulfuric acid and 18% sodium sulfate at approximately 45° C. The films after regeneration were thoroughly washed in hot water. They were then dried without plasticizer under clamped conditions so that shrinkage in area was prevented [4]. The regenerated cellulose films prepared from cellulose acetate were made by im-

TABLE I. Properties of Cellulose Films

	75° F., 35% RH	
	Viscose	Sapon. cellulose acetate
Tear resistance, g.	2.4	11.1
Impact resistance, Kg.-cm.	5.1	19.8
Elongation to break, %	5.0	43.3

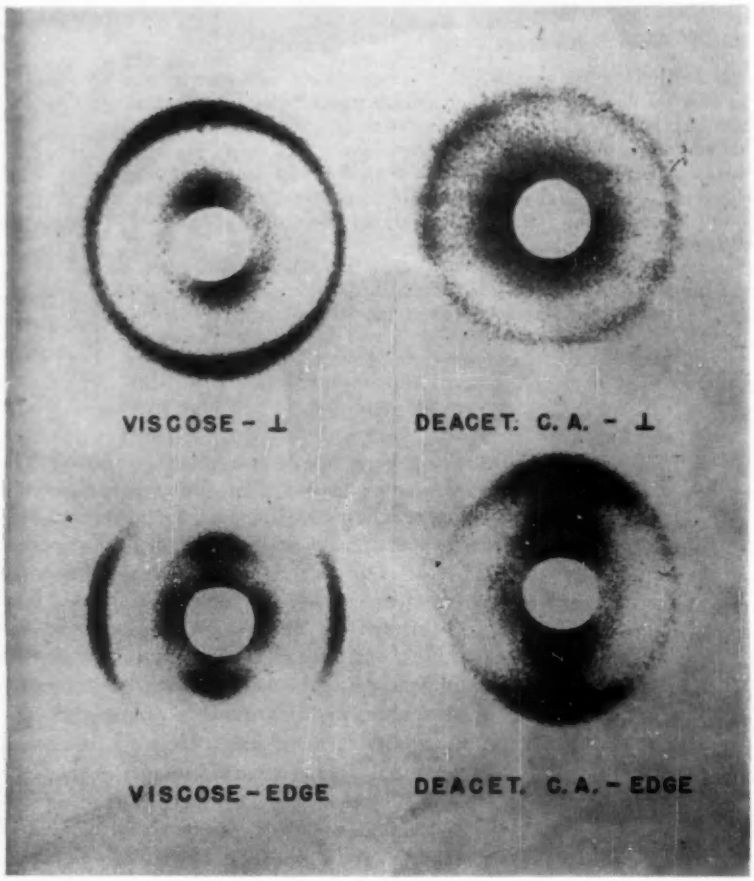

Fig. 1. X-ray diffraction patterns for viscose film and film from acetate.

mersing commercial cellulose acetate film in methanol containing 0.5% sodium methylate at room temperature for 30 min. After this period of time the film was washed thoroughly in hot water. Drying was the same as for the viscose films. The degree of swelling of the gel films expressed as the ratio of wet weight over dry weight was about 4.0 for the viscose film and about 2.1 for the film from cellulose acetate.

X-Ray Studies

X-ray diffraction examinations were made of these samples to reveal any large differences in crystallinity or in crystallite orientation. Diffraction diagrams were obtained photographically with a flat plate camera using a copper K-alpha source with a nickel filter. Both perpendicular and edge views were obtained. Curves of intensity versus Bragg angle were also obtained directly with the goniometer instrument equipped with a Geiger counter detector.

Diffraction patterns are shown in Figure 1. The level of crystallinity is apparently much lower in the film obtained from cellulose acetate. There is also evidence of a difference in crystallite orientation in these pictures. The perpendicular views indicate little, if any, uniaxial orientation in this film. Edge views show uniplanar orientation in both films. The film from cellulose acetate, however, does not show selective reflection from 101 planes evident in the film from viscose. In Figure 2 is shown a plot of intensity versus Bragg angle for these two films. This plot confirms the lower crystallinity and absence of selective orientation of 101 planes in the film from cellulose acetate. These aspects of structure are thoroughly discussed by Ott, Spurlin, and Grafflin [6] and by Sisson [7].

Acid Hydrolysis

The behavior of these films toward heterogeneous acid hydrolysis was also studied using the method of Battista [1]. Weighed film samples were hydrolyzed 15 min. in boiling 2.5 *N* hydrochloric acid. The residue was filtered off, washed thoroughly to remove acid, dried, and weighed. A portion of this dry residue was used for the measurement of 1% cupriethylenediamine viscosity and the degree of polymerization was calculated from this measurement. Table II summarizes the data obtained by acid hydrolysis.

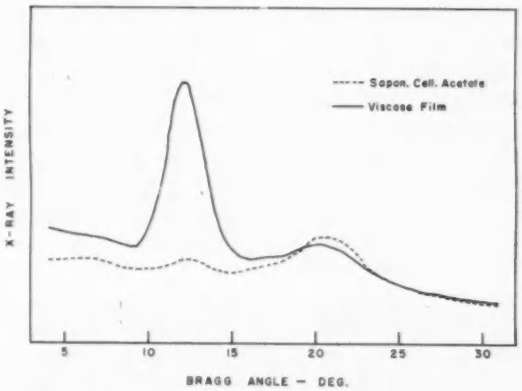

Fig. 2. X-ray intensity versus Bragg angle for viscose and saponified acetate films.

It is clear that the film from cellulose acetate yields much less residue of lower leveling-off $\overline{DP}$ than does the viscose film. The greater accessibility and the lower leveling-off $\overline{DP}$ is additional evidence for less crystalline material and smaller crystallite size in the case of the film from cellulose acetate.

Differential Swelling and Lateral Order Distribution

A considerable amount of work has been done with differential swelling in caustic solutions to obtain information about the mass-order distribution of cellulose [3]. Most of these methods involve the swelling of cellulose in sodium hydroxide solution and then the determination of the degree of swelling by moisture regain of the dried sample or by increased accessibility to various chemical agents. A simple and reproducible gravimetric method for measuring the degree of swelling has been developed for films. The differential swelling curves so obtained, not corrected for solubility, give a relative picture of the mass-order distribution in the film samples which is useful in comparing experimental samples of cellulose film. The following procedure was used. Squares of film weighing between 0.2–0.3 g. were weighed to the nearest milligram. Each square was immersed in a sodium hydroxide solution

TABLE II. Acid Hydrolysis of Cellulose Films

	% Residue	Leveling-off DP
Viscose	81.8	32
Sapon. cellulose acetate	65.0	19

of different concentration for 1 hr. or longer. Concentrations were from 1 to 10% in 1% increments. The swollen films were removed carefully from the sodium hydroxide solution and were spread flat upon a glass plate. The excess sodium hydroxide solution was removed by wiping the surface gently with a rubber squeegee blade, repeating until no further liquid was removed. About three passes with the squeegee were required. The film was then transferred to a tared weighing bottle and the weight was recorded to the nearest milligram.

Weight increments were plotted as a function of sodium hydroxide concentration to obtain a differential swelling curve of cellulose film. In Figure 3 the reproducibility of this method is illustrated. This curve was obtained with two samples of experimental cellophane differing only in the speed in which they were produced on the casting machine. A difference in speed can be expected to change the orientation of the sheet but should have much less effect on crystallinity or lateral order. These two curves appear to be identical within the experimental error. Figure 4 shows a comparison of the differential swelling curves normalized to the same area which were obtained with the regenerated cellulose film from viscose and from cellulose acetate. In the films from cellulose acetate, the position of the maximum of the differential swelling curve has been shifted to a considerably lower caustic concentration. It was also of interest that this sheet almost dissolved in caustic which was over 8% in concentration. These results clearly indicate a lower degree of order in the film prepared from cellulose acetate. The viscose film apparently contained regions which required much higher caustic concentrations for swelling to occur.

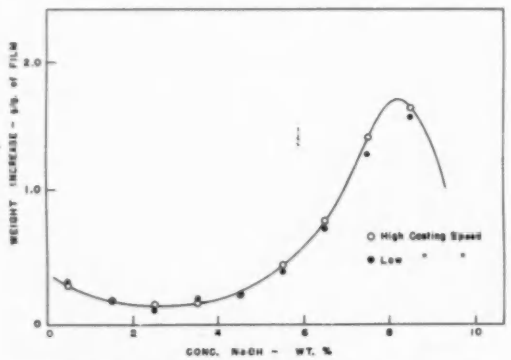

Fig. 3. Differential swelling of commercial cellulose films in caustic.

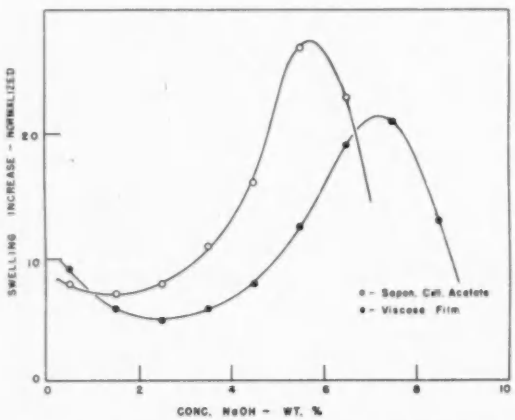

Fig. 4. Differential swelling of viscose and saponified acetate films in caustic.

Physical Failure

In an effort to elucidate the large differences in physical properties between these two films, studies were made of the mechanics of film failure in standard physical tests. The tear failure was chosen for study because of its relative simplicity and because of the fact that this test can be conducted at a rate slow enough to permit close observation. The test machine was a modified Elmendorf Tear Tester, which is used to measure the force required to propa-

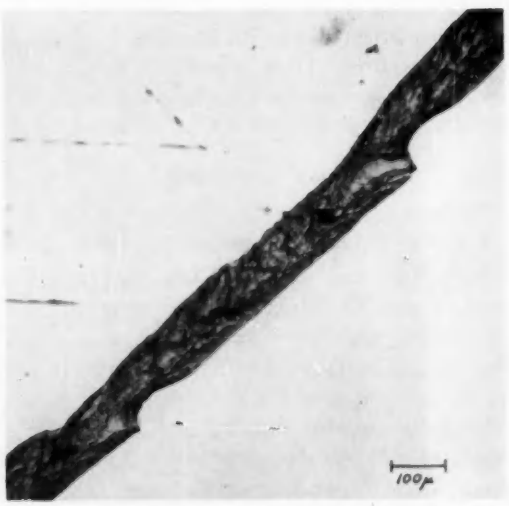

Fig. 5. Light micrograph; torn surface of viscose film.

gate a tear along 2 in. of film. Both the machine and the procedure are described elsewhere [2].

It was found that the new surface produced by tearing, examined edgewise along the axis of the tear, is a beveled edge whose angle appears to increase as the tearing strength of the film increases; the width of this new beveled surface decreases with increasing tearing strength. Films having a very low tear strength, such as viscose film without plasticizer, besides having a small tear angle, have a surface which appears in the light microscope as though it had a tendency to peel apart in layers. The film from cellulose acetate has a much narrower tear surface and appears to be fibrillar as though drawn in the direction of tearing. These two surfaces are shown in Figures 5 and 6.

For a study in greater detail, electron micrographs were made of the new tear surfaces of these films. Evaporated carbon replicas shadowed at 45° with chromium were made, using a parting layer. These replicas were very difficult to remove from the sample because of the high degree of roughness. The torn surface and the adjacent untorn surface of the film from viscose is shown in Figure 7. One sees a compact layer with some fibrillar character in which the individual fibrils are not too well defined. A few fibril ends protrude here and there. These were perhaps connecting links between adjacent layers in the structure. The diameter of the fibrils is fairly uniform and is approximately 0.05 μ. Orientation is not a striking feature in this structure. Figure 8 shows the torn surface and the adjacent untorn surface of the film from cellulose acetate. Again, a fibrillar structure is evident. The fibrils, however, are better defined, and many more fibril ends are seen. Also, the fibrils all tend to be pointing in the direction of the tear. It is not clear from this photograph whether the fibrils pre-existed in the undamaged structure or were formed by the tearing

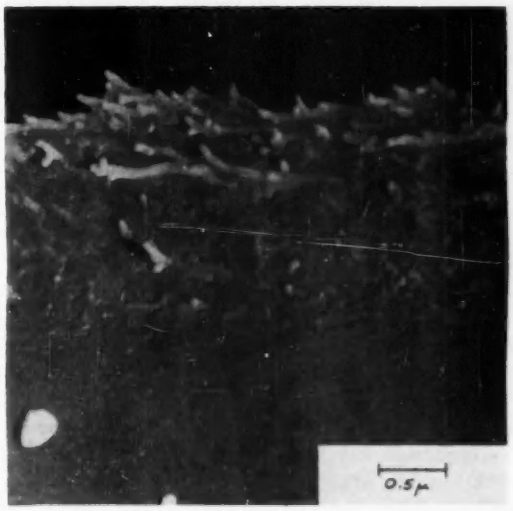

Fig. 7. Electron micrograph; torn surface of viscose film.

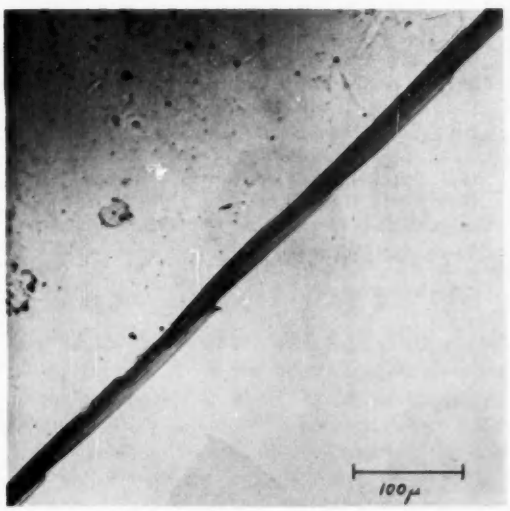

Fig. 6. Light micrograph; torn surface of saponified acetate film.

Fig. 8. Electron micrograph; torn surface of saponified acetate film.

process itself. Further work will be done to resolve this question.

Summary and Conclusions

An interpretation of these structural observations is offered as follows. One of the most significant structural differences between the films from viscose and from cellulose acetate is in their degree of ordering or crystallinity. The viscose film has the structure expected of a regenerated cellulose film which has not been oriented by drawing. A moderate degree of crystallinity together with uniplanar orientation of *b*-axes and of 101 planes is reasonable for a highly swollen gel network hooked together through crystallites which is forced to collapse in only one dimension during drying. This view is in accord with the observations of earlier workers on regenerated cellulose film from viscose [5].

The very low degree of order of the film from cellulose acetate is more surprising. It appears that the sequence of events through which the cellulose film is formed from acetate does not allow order to develop. The secondary acetate film, formed by solvent evaporation, lacks crystallinity because of partial substitution of hydroxyls by acetyl groups. The chains are probably highly entangled. Deacetylation in a nonaqueous system does not allow enough swelling to permit chains to disentagle and to become ordered. No stretch is imparted to the film at any stage. Fortisan is very similar in nature to this film with one important difference. Fortisan is drawn during preparation, which imparts parallel alignment to the chains. Regeneration then results in a highly ordered product [5]. After the regeneration of acetate film, swelling of the film in water is limited by the interaction of freed hydroxyl groups and, after the film is dried, ordered regions are apparently very small and poorly developed.

The effect of low order on increasing the extensibility and toughness is compatible with the theory that stresses are absorbed by deformation in the less ordered regions.

The appearance of fibrils of uniform size and their arrangement in dense tangled layers suggest that these may be basic units of the film structure. The layers are apparently weakly bonded in the thickness direction, as evidenced by the few fibril ends observed. This would explain the relatively easy delamination of the film and the broad torn surface.

The contrasting appearance of the tear surface of the film from acetate helps explain the much higher tearing strength of this film. Fibrils are in evidence, but they are parallel to the direction of the tear; fibril ends are much more numerous. Apparently considerable work was absorbed in orienting these fibrils and in breaking them.

Acknowledgments

The authors wish to express their appreciation to Dr. Gordon Patterson, Jr., E. I. du Pont de Nemours & Co., Inc., Film Research Laboratory, Experimental Station, Wilmington for the preparation of the x-ray diffraction studies. They also wish to express their appreciation to Mr. Joseph Godlewski, E. I. du Pont de Nemours & Co., Inc., Central Research Department, Experimental Station, Wilmington for the preparation of the electron micrographs.

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Cross-Linking of Partially Cyanoethylated Cotton[1]

Part III: Acid Scouring of Amidoximate and Subsequent Formaldehyde-Curing

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Abstract

By 0.1–0.5% hydrochloric acid scouring, which has been shown to prevent the discoloration of the amidoximates of partially cyanoethylated cotton fabrics in the previous paper, it was found that the amidoximate hydrochloride salt might be formed. In comparison with unscoured amidoximates, the scoured material, even when formaldehyde-cured under noncatalyzed neutral conditions, with or without tension, had exceedingly improved crease resistance without much loss in tensile strength, elongation, and tear strength. The softness of cotton was retained. It was deduced that the amidoximate hydrochloride might presumably split off hydrochloric acid and act as a self-catalyst in the formaldehyde-curing.

Introduction

In the previous publication from our laboratory, it was reported that the amidoximation products of partially cyanoethylated cotton fabrics with neutralized aqueous hydroxylamine were prevented from discoloring to a certain degree by scouring with about 0.5% hydrochloric acid in the washing process [1]. In the present paper, moreover, it was found that the acid scouring of amidoximates might play an important role in subsequent formaldehyde-curing: the formation of amidoxime hydrochloride salt and its self-catalytic action in formaldehyde-curing.

Experimental

Materials

Partially cyanoethylated cotton fabrics (calico cloth 30's) containing 2.62% nitrogen were used.

Amidoximation

The partial amidoximation of cyanoethylated cotton was carried out in the neutralized aqueous hydroxylamine (pH 7.5, 96–97° C., 20 min., and 40–48 liquor ratio) as in the previous report. The reaction products were washed thoroughly with water either with or without the process of acid scouring by 0.01–1.0% hydrochloric acid (20° C., 10 or 20 min., and 180 or 200 liquor ratio). Also, acid scouring under tension was tried.

Determination of Bound Hydrochloric Acid

For the acid scoured samples, the determination of bound hydrochloric acid was attempted by means of the back titration method, using 1/20 *N* NaOH and HCl, with phenolphthalein indicator.

Formaldehyde-Curing

The amidoximates of cyanoethylated cotton fabrics were soaked for 10 min. at room temperature in the following three kinds of solutions containing 12% formaldehyde which were prepared from a commercial grade formaline.

1. Nothing added (pH 4.54–4.60)
2. Neutralized with sodium hydroxide (pH 7.00–7.25)
3. Containing 0.5% ammonium acetate as cure-catalyst (pH 4.30–4.32)

The soaked fabrics were pressed out to about 100% pickup of the solution and cured for 10 min. at 110–120° C. under or without tension. The cured fabrics were washed with hot water.

Test Procedures

All tests of the mechanical properties were carried out as in the previous paper.

[1] Presented at the 8th lecture-meeting of the Japan Cotton Technical Institute, Osaka, April 6, 1960.

Discussion and Results

Effects of Acid Scouring on Physical Properties of Cured Fabrics

Of the amidoximation products prepared simultaneously, one part was only washed with water and another was successively scoured by 0.5% hydrochloric acid (20° C., 10 min., and 180 liquor ratio) and rewashed thoroughly with water. The former gave 3.34% N and a slight yellowish blue discoloration; the latter gave 3.26% N and hardly any discoloration. After padding in the formaldehyde solution (nothing added, neutralized with sodium hydroxide, or containing 0.5% ammonium acetate), the amidoximates were cured for 10 min. at 115–120° C.

TABLE I. Effects of Acid Scouring of Amidoximates on Physical Properties of Formaldehyde-Cured Fabrics

Sample	Kind of formaldehyde solution for curing	Nitrogen content, %	Tensile strength, Kg./cm.	Elongation, %	Crease resistance (T.B.L.), %
Unmodified cotton boiled with water	—	—	7.20	12.8	54.3
Cyanoethylated cotton boiled with water	—	2.62	8.25	13.2	57.0
Amidoximate washed with water	uncured	3.34	7.62	12.4	67.0
	neutralized, pH 7.25	—	6.00	10.4	72.8
	nothing added, pH 4.54	—	5.40	10.3	80.4
	0.5% ammonium acetate, pH 4.30	—	5.00	10.0	82.3
Amidoximate scoured by 0.5% HCl	uncured	3.26	7.20	13.6	68.9
	neutralized, pH 7.25	—	4.24	12.0	93.1
	nothing added, pH 4.60	—	4.06	13.2	92.0
	0.5% ammonium acetate, pH 4.32	—	3.80	12.0	94.1

TABLE II. Effects of Concentration of Hydrochloric Acid Used for Scouring of Amidoximates on Physical Properties of Formaldehyde-Cured Fabrics

Sample	Composition of scouring liquor of amidoximate	Tensile strength, Kg./cm.	Elongation, %	Crease resistance (T.B.L.), %	Area shrinkage, % by	
					Scouring	Curing
Unmodified cotton boiled with water	—	7.12	13.0	50.8	—	—
Cyanoethylated cotton boiled with water	—	9.02	13.2	58.8	0	0
Amidoximate cured with neutralized formaldehyde	water	6.03	12.2	74.5	0.2	1.4
	0.01% HCl	5.23	11.8	84.1	1.1	1.8
	0.05% HCl	4.83	10.4	89.5	2.6	2.1
	0.1% HCl	4.40	10.2	90.0	4.5	1.5
	0.3% HCl	4.08	10.0	93.3	4.7	1.4
	0.3% HCl + 0.5% Na_2CO_3	5.75	13.0	71.4	4.0	0
	0.5% HCl	4.10	10.0	93.2	3.8	2.2
	1.0% HCl	4.02	10.2	92.7	4.0	1.7
	1.0% HCl + 0.5% Na_2CO_3	5.72	12.8	72.1	3.5	0.1

The tensile strength, elongation, and crease resistance of these cured fabrics were measured and are shown in Table I. It is observed that the crease resistance of the amidoximates washed only with water is slightly improved by neutral formaldehyde-curing and significantly improved to nearly the same extent by the non-catalyzed or acid-catalyzed formaldehyde-curing without so great a corresponding loss in the strength and elongation. From the above results, it seems to be doubtless that a slight acidity in a commercial grade formaline might have a catalytic action for the intermolecular methylene cross-linking between amidoxime or hydroxamic acid groups [1, 4].

On the other hand, it is noteworthy that the crease resistance of the amidoximates scoured by hydrochloric acid is distinctly more improved than any of the former even by the neutral formaldehyde-curing; moreover, the improvement is independent of the presence or absence of catalyst in the formaldehyde solution. However, the loss in tensile strength is somewhat greater. Since it has been known that the monohydrochloride salt is formed in the smaller-molecule amidoxime compounds such as acetoamidoxime or propionoamidoxime [2], there is a possibility that the partially amidoximated cotton cellulose also can form the hydrochloride salt by acid scouring. If so, the bound hydrochloric acid may presumably be split off and act as a stronger catalyst than any others in the formaldehyde-curing. It is also possible that the very weak acid groups of oxime or hydroxamic acid groups have been made completely free by acid scouring and have displayed a catalytic action to some extent; however, these acid groups are considered to be too weak to give the catalytic effects obtained above [3, 5]. Further work dealing with these catalytic actions is in progress. It is interesting that the acid scouring of amidoximates brings about not only a prevention of discoloration but a catalytic action of intermolecular cross-linking.

Effects of Concentration of Hydrochloric Acid Used for Scouring

The partially amidoximated cotton fabrics were prepared under the same condition as mentioned above, washed with water, pressed out to about 100% pickup of water, scoured by 0.01, 0.05, 0.1, 0.3, 0.5, and 1.0% hydrochloric acid (20° C., 20 min., and 200 liquor ratio), and rewashed thoroughly with water. The scouring by hydrochloric acid over 0.1% in concentration resulted in hardly any discoloration. A portion of the amidoximates scoured by 0.3 and 1.0% hydrochloric acid was soaked in 0.5% sodium carbonate (20° C., 30 min., and 200 liquor ratio) and washed with water. These treated fabrics were cured for 10 min. at 110–115° C. using the neutralized formaldehyde solution (pH 7.0). The shrinkage of fabrics caused by acid scouring and formaldehyde-curing was measured in comparison with the cyanoethylated cotton fabrics and shown in Table II and Figure 1 with mechanical properties.

It is observed that crease resistance increases rapidly with increasing concentration of hydrochloric acid for scouring and tends to level over 0.2% concentration; the loss of tensile strength and elongation

TABLE III. Effects of Acid Scouring and Formaldehyde-Curing under Tension on Physical Properties

Sample	Nitrogen content, %	Tensile strength, Kg./cm.	Elongation, %	Crease resistance (T.B.L.), %	Tear strength, Elmendorf's unit	Clark's stiffness, L^3W	Area shrinkage, %
Unmodified cotton	—	7.20	13.0	51.4	45.8	2.03	—
Cyanoethylated cotton	2.62	8.14	15.7	54.9	38.5	2.24	0
Amidoximate washed with water	3.29	7.06	12.6	65.0	37.0	1.78	0.4
Scoured by 0.1% HCl							
Without tension	3.16	7.08	12.7	66.9	35.2	1.90	6.9
Under tension	—	6.99	10.2	70.6	34.8	1.87	0.2
Scoured by 0.1% HCl and cured with neutral formaldehyde							
Without tension	—	5.02	12.0	92.4	23.5	2.04	8.8
Under tension	—	5.21	9.8	89.8	26.2	2.16	0

shows a good correspondence with the improvement of crease resistance. Shrinkage caused by curing is not great. On the contrary, when the alkali treatment after acid scouring was carried out, the crease resistance, tensile strength, and elongation of amidoximates were changed by curing only to the same extent as these of amidoximates washed with water, in spite of the presence of fabric shrinkage. This fact seems to show that the amidoximate hydrochloride salt has been formed by acid scouring and the significant improvement of crease resistance by formaldehyde-curing has taken place not by fabric shrinkage but by a catalytic action of the split hydrochloric acid.

Acid Scouring and Formaldehyde-Curing under Tension

In order to know the effects of fabric shrinkage on the mechanical properties of treated fabrics, acid scouring and formaldehyde-curing under tension to the extent of no shrinkage were carried out. The amidoximates were prepared under the same condition of reaction as mentioned above. After the fabrics were washed with water and pressed, scouring with 0.1% hydrochloric acid (20° C., 20 min., and 200 liquor ratio), rewashing, and drying were all carried out under tension. The curing (110–115° C., 10 min.) and subsequent washing and drying also were carried out under tension, using the neutralized formaldehyde solution (pH 7.0). The mechanical properties are shown in Table III in comparison with these of fabrics treated without tension.

It was found that the crease resistance, tensile strength, elongation, tear strength, and softness were almost unaffected by tension in acid scouring and curing. This result shows doubtless that the improvement of crease resistance has not been attributed to the fabric shrinkage by acid scouring.

Determination of Bound Hydrochloric Acid

The amidoximates obtained under the same conditions as mentioned above were scoured by 0.01 0.1, 0.25, and 1.0% hydrochloric acid (20° C., 20 min., and 200 liquor ratio). The nitrogen contents were 3.50% for the unscoured and 3.18% for the 0.25% HCl-scoured samples. With about 0.5 g. of the samples, the total amounts of acidic groups were determined by the back titration method using phenolphthalein indicator. The indicator method might be strictly inaccurate because of the presence of weak acid groups of hydroxamic acid and amphoteric amidoxime groups [3, 5]. However, since the titration showed the relatively distinct end point, it should seem to give a certain relative value at least. The total amounts of acidic groups in amidoximates (g.equiv./g.) obtained thus are shown in Figure 2, at varying concentration of acid for scouring.

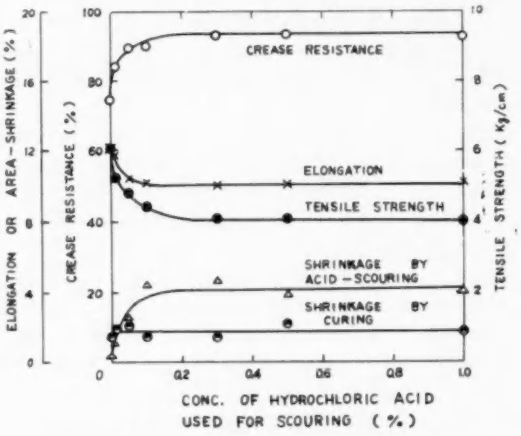

Fig. 1. Effects of concentration of hydrochloric acid used for scouring of amidoximates on physical properties of formaldehyde-cured fabrics.

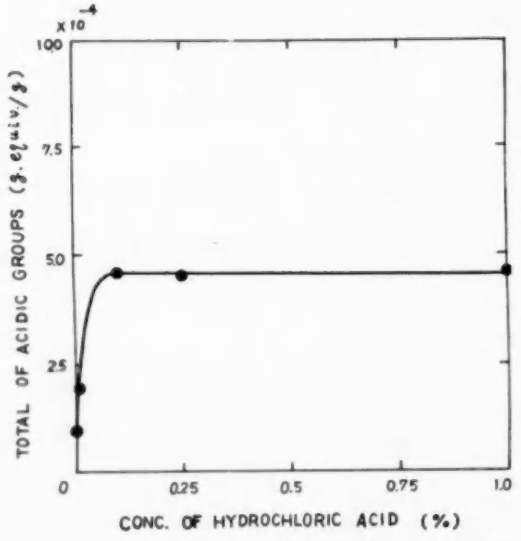

Fig. 2. Total amounts of acidic groups in amidoximates at varying concentration of hydrochloric acid used for scouring.

It is noteworthy that the total amounts of acidic groups increase rapidly with increasing concentration of acid and reach an equilibrium value over 0.1% acid corresponding with the improvement of crease resistance after curing. This result supports powerfully our consideration predicated above.

In the alkali solution with which the acid-scoured amidoximate was treated, the presence of chloride ions was distinctly proved qualitatively. Therefore, assuming that the amounts of acidic groups obtained for the water-washed sample (0.93×10^{-4} g.equiv./g.) and the acid-scoured sample (as the equilibrium value, 4.56×10^{-4} g.equiv./g.), approximately correspond to all the hydroxamic acid groups and the total of hydroxamic acid and bound hydrochloric acid respectively, the bound hydrochloric acid is estimated to be 3.63×10^{-4} g.equiv./g. as the equilibrium value. Also, on the assumption that the value corresponds to all the amidoxime groups, the composition of the amidoximate is computed to be 8.4, 2.2, and 0.6 mole percent for $-CN$, amidoxime, and hydroxamic acid groups respectively. The nitrogen content calculated from the above composition is 3.05% and agrees approximately with the experimental value of the acid-scoured sample (3.18%). If the total amounts of acidic groups found above correspond to all the hydroxamic acid groups, the contents of $-CN$, amidoxime, and hydroxamic acid groups should be 5.6, 2.8, and 2.8 mole percent respectively. It seems to be certain that the true composition is between the former and the latter. To ascertain this result, the analysis by means of the conductive or potentiometric titration and the determination of chloride ions is now in progress.

Conclusions

By hydrochloric acid scouring and subsequent non-catalyzed neutral formaldehyde-curing under or without tension, crease resistance of the amidoximates of partially cyanoethylated cotton fabrics was remarkably improved without much loss in tensile strength, elongation, and tear strength; the softness of unmodified cotton was retained. It was found that the amidoximate hydrochloride salt might be formed by acid scouring. It is probable that the amidoximate hydrochloride splits off hydrochloric acid and acts as a self-catalyst in the formaldehye-curing. The facts that the acid scouring of amidoximates brings about not only discoloration prevention but a catalytic action of intermolecular cross-linking are interesting.

Acknowledgment

The authors are indebted to the Japan Cotton Technical Institute, Osaka, for their financial assistance. We are also grateful to Professor W. Tsuji and Dr. R. Kitamaru of the Institute for Chemical Research, Kyoto University, for preparing partially cyanoethylated cotton fabrics for us.

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Letter to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Fiber Alignment Device

United States Department of Agriculture
July 18, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The standard method of determining fiber diameter and distribution by the microprojection method is both time-consuming and tedious, since the fibers lie at various angles on the slide, making it necessary to rotate the wedge scale considerably in order to measure each fiber properly. To develop a means of aligning the fibers for greater ease and speed of measurement, The Special Instruments Laboratory, Knoxville, Tennessee, working under contract with the U. S. Department of Agriculture, Sheep and Fur Animal Research Branch, Beltsville, Maryland, produced an electrostatic fiber alignment device which consists of three parts.

1. Chassis—a box containing a high-voltage transformer, a sample chamber, and an indicating lamp.
2. Slide holder—a tray used to keep the slide and mounting medium from contact with the bottom of the sample chamber.
3. Cover plate—a plate used to protect the operator, since high voltage cannot be applied unless the cover is in place.

In order to use the device, the operator prepares a slide in accordance with instructions in "Standard Specifications and Method of Test for Fineness of Wool Tops—ASTM Designation: D472-56" up to the mounting of the fibers. The fiber pieces are dispersed in Permount or in an immersion oil and a cover slip is placed in position. The slide is then placed in the slide holder, which is inserted in the device. The cover plate is placed on the device, and the fibers begin to align immediately. Alignment is completed and the medium sets sufficiently while a second slide is being prepared. Measurements are made and recorded as outlined in the above-mentioned specification.

Permount had not been previously used as a medium for the mounting of fibers for fineness determination. Results obtained at Beltsville indicated that mean diameter and distribution were not affected by use of Permount in place of the mineral oil required in the specification. For additional comparisons, twelve samples of wool top from individual fleeces were sent to the Wool Associates of the New York Cotton Exchange, Boston, Massachusetts, to be measured for fineness, using Permount and immersion oil as media.

The data in Table I indicate that either Permount

Fig. 1. Picture of device.

or immersion oil used by the Wool Associates laboratory can be satisfactorily used as a mounting medium for fineness determinations. The report from the Wool Associates stated that the mounting media used in obtaining these data had no bearing on the diameter of the wool fibers.

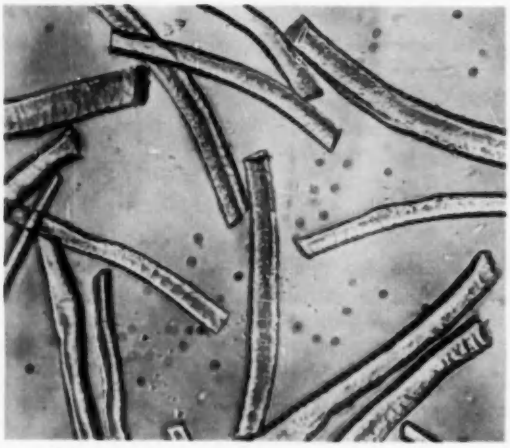

Fig. 2. Picture showing fibers in mineral oil.

Fig. 3. Picture showing fibers aligned in immersion oil.

TABLE I

Lot no.	Mounting medium	Average diameter	Distribution					
			10–25	10–30	25.1+	30.1+	40.1+	50.1+
7961	Oil*	23.38		90.50		9.50	1.50	
	Permount	23.34		89.50		10.50	.50	
7968	Oil	22.82		95.75		4.25	.50	
	Permount	22.98		96.00		4.00	.50	
8033	Oil	21.02	84.50	97.50	15.50	2.50		
	Permount	20.94	89.00	97.50	11.00	2.50		
8143	Oil	23.72		90.50		9.50	1.00	
	Permount	24.06		92.00		8.00	1.00	
8165	Oil	27.91		72.25		27.75	2.00	
	Permount	28.14		70.00		30.00	1.00	
8184	Oil	24.06		86.00		14.00	1.00	
	Permount	23.26		90.50		9.50	1.00	
8204	Oil	26.94		83.25		16.75	1.25	.25
	Permount	26.62		83.50		16.50	1.00	.00
8223	Oil	29.18		61.75		38.25	4.75	.25
	Permount	29.21		63.50		36.50	4.00	.25
8236	Oil	24.77		88.25		11.75	.50	
	Permount	25.42		86.00		14.00	.50	
8267	Oil	21.33		96.25		3.75	.25	
	Permount	21.18		97.00		3.00	.00	
8266	Oil	24.82		85.00		15.00	1.50	
	Permount	25.00		85.75		14.25	1.25	
8306	Oil	26.37		77.75		22.25	1.25	
	Permount	27.22		75.00		25.00	3.00	
		24.69 Average all oil tests						
		24.78 Average all Permount tests						

* Immersion oil used by Wool Associates.

The Wool Associates operators found that fibers in immersion oil were more distinct than those in Permount. This particular immersion oil was then successfully tried with the device at Beltsville. Both laboratories found that dispersion of fibers is improved, with few, if any, intersecting fibers, when the alignment device is used with either medium. For visual measurement by the microprojection method, alignment of the wool fibers lessens the number of movements of the wedge scale in determining the fiber diameter, thereby increasing the operator's speed in measurement.

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Book Reviews

Natural and Synthetic Fibers Yearbook 1959. Milton Harris and H. Mark, editors. New York, Interscience Publishers, Inc., 1960. 1339 pp. Price $60.00.

Reviewed by Richard K. Toner, Textile Research Institute, Princeton, New Jersey

This book is a collection of abstracts of papers published in 1959 and concerned with the properties and behavior of natural and man-made fibers. These abstracts were originally issued as Numbers 1–12, Series II, Volume VI of Natural and Synthetic Fibers Literature and Patent Service. They have been prepared with the cooperation of Harris Research Laboratories and the Institute of Polymer Research.

As users of previous volumes are aware, the abstracts are not simply short summaries of papers but frequently 2–3 page outlines of the article. Each abstract is organized under topic headings such as Author(s); Author Address; Journal of Original Publication; Title; Purpose or Objective; Apparatus, Materials and Methods; Procedures; Results and Discussion; Conclusions and Recommendations. Important figures and tables are frequently reproduced. Both a subject and author index are included at the end of the volume.

There can be no question of the value of this volume to the serious investigator. Although the necessarily high price precludes its purchase by most individuals, no library can afford to be without it.

The Hydrogen Bond. George C. Pimentel and A. L. McClellan. San Francisco and London, W. H. Freeman and Co., 1960. xii + 475 pages. Price $11.40.

Reviewed by Walter Lobunez, Textile Research Institute, Princeton, N. J.

This book is the first comprehensive and critical review that unifies the mass of literature concerned with the hydrogen bond. An annotated bibliography of 2240 references indicates the amount of work performed by the authors; it can be very helpful for clarifying the historical aspects of the subject. A wealth of experimental facts is compiled, summarized, and critically reviewed. Many helpful figures and tables are included in the text, and almost 40 pages of tables in appendices contain the data

on thermodynamic properties and on equilibrium constants for the H-bond formation, with references to the source of the data.

In 157 pages the authors deal with the advantages and the limitations of the known methods for detection of the H-bond. The discussions related to the infrared techniques are especially instructive and can be very helpful to students, indicating at the same time a profound familiarity of the authors with the topic. In two chapters the authors deal with thermodynamic properties and present a short introduction to the theory of the H-bond. The mathematical detail is omitted.

A relatively large part of the book is about the different kinds of H-bonds and about different systems involving the H-bond. The treatment of borderline cases including chloroform, acetylenes, and borohydrides is especially interesting. Despite the slight evidence provided by the normal band width of ν_s and the direction of the NMR chemical shift in support of the conventional view that the electron-deficient borane structures cannot involve the same bonding situation as the H-bond, the authors are inclined to think that the pattern of similarity between the borane bridge band and the H-bond encourages the expectation that a single theoretical framework for boranes and H-bonds will suffice. The discussion of specific points that the study of H-bonding presents in some practical systems, for instance in cellulosic and in other fibers, is not extensive, but the knowledge about general facts and the theory of the H-bond that this book helps to establish can be very useful to a scientist for mastering such problems.

Fairchild's Dictionary of Textiles. Stephen S. Marks, editor. New York, Fairchild Publications, Inc., 1959. 627 pages. Price $25.00.

Reviewed by L. Rebenfeld, Textile Research Institute, Princeton, New Jersey

"Fairchild's Dictionary of Textiles" is a greatly expanded outgrowth of "Harmuth's Dictionary of Textiles." Compiled as a staff project of Fairchild Publications, it contains more than 12,000 entries dealing with all phases of textiles. Particular emphasis is given to definitions of highly specialized domestic and foreign textile fabrics and finishing treatments. The synthetic fibers are included in this work, both in generic and trademark classifications. Unfortunately, due to the publication date, exact conformance of generic fiber definitions with the FTC was not possible.

Its very wide coverage of the textile field, rather than its depth and accuracy of definitions, makes this dictionary a worthwhile addition to libraries specializing in textiles.

Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry. L. M. Jackman. London, Pergamon Press, Ltd., 1959. 134 + XII pages.

Reviewed by Askel A. Bothner-By, Mellon Institute, Pittsburgh, Pa.

This short book, written by an organic chemist for organic chemists, succinctly summarizes the theory and most of the presently available empirical knowledge concerning the application of high-resolution NMR spectroscopy to the determination of the structures of organic compounds. There are seven chapters: 1. Introduction and Historical Review; 2. The Theory of Nuclear Magnetic Resonance Spectroscopy; 3. The Experimental Method; 4. The Correlation of the Chemical Shift with Molecular Structure: Hydrogen Bound to Carbon; 5. The Correlation of the Chemical Shift with Molecular Structure (A. Protons Attached to Elements Other than Carbon, B. Nuclear Magnetic Resonance of Isotopes Other than Carbon); 6. The Interpretation of the Spectra of Complex Organic Molecules; and 7. Diamagnetic Anistropy and Stereochemistry.

Dr. Jackman mentions in his preface that it is his intention to keep physical and mathematical background at a minimum, but to present the essential physical principles descriptively, and further to present such useful empirically correlated data as are now available. He succeeds reasonably well in the first goal, admirably in the second.

Parts of the theory underlying nuclear magnetic resonance are of such uncompromising mathematical and physical nature that it is a Herculean task to present it in nonmathematical guise, still retaining a reasonably rigorous aspect. Other parts (for example, the theory of diamagnetic shielding) can be presented in this way with clarity and vigor, and Dr. Jackman has often done so. These discussions will certainly be particularly valuable to the organic chemist.

It is inevitable that this book, appearing at this time, will be compared with the two other recently published texts in this area, J. D. Roberts' "Nuclear Magnetic Resonance" and J. A. Pople, W. G. Schneider, and H. J. Bernstein's "High Resolution Nuclear Maguetic Resonance Spectroscopy." On the whole the introduction to the theory is both more nearly rigorous and easier to understand in Professor Roberts' book. The book by Drs. Pople, Schneider, and Bernstein is much more exhaustive, and makes considerable mathematical demands on the reader. Dr. Jackman's collection and tabulation of useful shift data is extremely handy, and those who presently use NMR will certainly want to own this book for the valuable tables of Chapters 4 and 5 as well as some of the other features. For the organic chemist seeking an introduction to the field, reading Dr. Jackman's and Dr. Roberts' books concurrently is probably the best prescription (both are short). For the organic chemist who intends to work seriously in this area, the book by Drs. Pople, Schneider, and Bernstein is still the *sine qua non*.

Soap Films. Studies of Their Thinning. Karol J. Mysels, Kozo Shinoda, and Stanley Frankel. New York, Pergamon Press, 1959. 116 pages. Price $7.50.

Reviewed by Anthony M. Schwartz, Harris Research Laboratories, Inc., Washington 11, D. C.

It is a peculiar circumstance of our present-day chemical world that few if any journals can accept discursive accounts of extensive research works, particularly if they include related discussions of background and theory. Since certain studies lose their impact when split up into a series of terse papers, some investigators prefer to present a major work in monograph form. "Soap Films" is a monograph of this type, although it is shorter and more limited in scope than most, and might better be likened to an unusually erudite dissertation or thesis. It is concerned with the behavior of soap films (a generic term here; surfactants are included) as they become thinner.

Most of the experimental studies described in the text consist in careful, well-instrumented observations of single soap films, supported either by wires or by their junctions with other soap films. These films become progressively thinner, due either to drainage caused by gravity, to capillarity effects at the boundaries, or to evaporation. The film thickness can be monitored with great precision by optical means. The authors classify and describe soap films in four major categories (rigid, mobile, irregular mobile, and black), each with its characteristic structure, drainage, and thinning behavior. The thinning mechanisms for each type of film are discussed clearly and succinctly. The most important original contributions concern the irregular mobile films and the black films. Considerable theoretical discussion is interspersed in the descriptive chapters, and two complete chapters of the total seven are devoted to the authors' development of a hydrodynamics of film behavior.

An excellent, well chosen bibliography of over 300 references greatly enhances the value of the book to the less specialized reader. It remains in essence, however, the presentation of an important but limited research contribution. It will be of primary value to the authors' fellow researchers and to other specialists in the field of foams and liquid films.